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CRACK-FREE CHROMIUM FROM CONVENTIONAL PLATING BATHS

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EXTRACTION METALLURGY DIVISION

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Crack-Free Chromium from Conventional Plating Baths

J. C. Saiddington and G. R. Hoey*

ABSTRACT

The formation of cracks in chromium coatings obtained from conventional baths at the bright plating range of current density and temperature can be reduced or eliminated by employing controlled plating interruptions. The interruptions, to be effective, must a) allow dissipation or cause deactivation of the cathode film and b) be frequent enough to prevent the incremental increases of the deposit thickness associated with the formation of sets of cracks. The technique puts no restriction on i) the type of plating interruptions as long as they meet the above specified conditions, ii) the exact control of their frequency, iii) the concentration of the plating bath, iv) the current density and temperature, v) the thickness of the crack-free coating and vi) the type of the substrate, but requires knowledge of the critical thickness at which formation of cracks begins. Plating interruptions may cause loss of luster; appearance deteriorating as the frequency of interruptions increases. With interruptions suitably chosen, chromium becomes crack-free and remains bright on the microscale; thus is acceptable for buffing.

THE FORMATION OF CRACKS in conventional chromium deposits does not occur until the coating thickness exceeds a level of about 0.5 μm[1-3]. As the deposit grows thicker a network of cracks develops[4].

Jones and Saiddington[5] have observed that the network of cracks, seen in thicker deposits, does not develop instantly nor continuously but rather in a step-wise manner at definite intervals of time at which the cracks increase in density with each new set of cracks forming, until a certain maximum is reached.

At the conventional current density (2200 A/m^2) and temperature (45°C) sets of cracks form at intervals of time of between 2.5 and 3.5 min, which for purposes of discussion gives an average of about 3 min.

Examination of cross sections of thick chromium deposits revealed striations that correlated well with the periodic formation of cracks[6]. Similar observations were made earlier by Brittain and Smith[7], who found that the formation of cracks in thick deposits after many hours of plating was taking place at intervals of time which were found, more recently, to be essentially the same as those observed at the beginning of development of cracks[5].

The evidence suggests that the formation of cracks is associated with incremental increases of the deposit thickness which at the conventional plating rates of 0.25 μm/min is related to an average deposit thickness increase of 0.75 μm and that the formation of cracks will be impeded if the plating is stopped before this critical thickness is reached. (In practice, allowance must be made for occasional formation of cracks at lower thicknesses).

Investigations of the initial stages of chromium deposition[8] have shown that the formation of initial cracks is preceded by a continuous decline of gas evolution during the final shift of potential to the value of steady state deposition, and that this phenomenon may be attributed to some physico-chemical transformations in the liquid layer adjoining the cathode surface that brings about the formation of an adsorbed cathode film.

The existence of the cathode film is essential for the progress of the chromium deposition step to continue[9]. To stop the plating progress it is essential that the cathode film be removed or deactivated. Restarting plating thereafter will require that the film be re-established and that this process will interrupt the continuity of the deposit growth. If the interruptions are frequent enough to prevent the incremental increase of the deposit thickness associated with the formation of cracks, their incidence will be reduced or completely eliminated, depending on the spacing of the interruptions.

Since the average critical thickness, under the plating conditions mentioned above, is about 0.75 μm, significant decline of the formation of cracks should be expected with interruptions at this thickness level.

Experimental results are shown in this paper to agree with the above postulates. Chromium coatings have been produced at conventional current density and temperature with decreased or eliminated incidence of crack formation, using plating interruptions at intervals of time equal to or smaller than the average required to plate critical thickness of chromium.

Similar results were obtained at lower current densities and in a more concentrated bath indicating that the principle of controlled interruptions is applicable more universally, provided adjustments are made for different plating rates and different critical thicknesses that may be operative under different plating conditions.

EXPERIMENTAL

Preparation of the Substrate

All tests were made with 21 x 75 mm coupons cut from mild steel panels, in the as-rolled condition, or from Hull cell test panels. The panels with a roll mill surface finish were approximately 0.8 mm thick, thus providing a rigid substrate base. They were used exclusively for the deposition of chromium on bare steel. The Hull cell test panels were about half as thick (0.4 mm) and were, therefore, more pliable. They were prefinished to a reasonably lustrous appearance that was protected by the manufacturer by a thin zinc coating against abrasion and soiling. These panels were used for deposition of chromium on bare and nickel-plated steel.

Chromium plating on panels with roll mill finish was preceded by vapor degreasing with trichloroethylene, and by wet blasting with 220-grit aluminum oxide slurry. Just before plating, the specimens were activated with a 5-sec dip in 1:1 HCl acid followed by a thorough rinse in distilled water.

The Hull cell test panels did not require any cleaning procedure since they were precleaned and protected by a thin zinc coating. The zinc was removed, just before

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plating, by a 5-sec dip in 1:1 HCl acid, followed by a rinse in distilled water. This procedure was adequate to provide good adhesion for both nickel and chromium.

When chromium was deposited on nickel-plated specimens, they were first cathodically cleaned in an alkaline solution containing 45 g/l of NaOH and 30 g/l of Na_2CO_3. Then they were activated by a short dip (10-15 sec) in an 8 per cent sulfuric acid bath containing 1 g/l of KI.

Plating Conditions

a) Chromium

Practically all chromium coatings were obtained from the standard plating bath containing 250 g/l of CrO_3 and 2.5 g/l of H_2SO_4 at a current density of 2200 A/m^2 and a temperature of 45°C. Some platings were also made at a C.D. of 1100 A/m^2 and a temperature of 40°C in the conventional bath; and in a more concentrated bath containing 400 g/l of CrO_3 and 4 g/l of H_2SO_4.

At the conventional C.D. (2200 A/m^2) and temperature (45°C), it takes roughly 1 min to plate 0.25 μm of chromium. At 1100 A/m^2 and 40°C the plating rate is 0.10 μm/min in the conventional bath and 0.062 μm/min in the concentrated bath[10]. All plating rates were confirmed by repeated thickness measurements of conventional and crack-free deposits.

The plating bath was contained in a rectangular Pyrex glass vessel (20 x 12.5 x 14 cm) with 2 l capacity, and was immersed in a constant temperature bath. Curved lead anodes (5 x 11.5 x 12.5 cm) were placed at both ends of the vessel while the 21 x 75 mm coupons were kept in the geometrical center by means of a specially made jig which also served to protect the edges from excessive build-up of the deposit. Reasonably uniform coatings were obtained in this way on both sides of the specimens with continuous and interrupted plating.

b) Nickel

Nickel was plated in a circular vessel of 2 l capacity using 2 pure nickel anodes heavily bagged, and employing efficient mechanical agitation. The coupons were plated on both sides, either one at a time, or in pairs by means of a jig specially made for this purpose.

The nickel plating was carried out from a bath containing 240 g/l of $NiSO_4.6H_2O$, 45 g/l of $NiCl_2.6H_2O$, 30 g/l of H_3BO_3, 7.5 g/l of 1.5-naphthalenedisulfonic acid, and 0.075 g/l of sodium lauryl sulfate. The temperature of deposition was 55°C and the current density 400 A/m^2. The hydrogen ion concentration at *p*H 3.5 was periodically adjusted by addition of HCl or H_2SO_4. The deposit obtained had an excellent mirror-like appearance. Nickel was deposited at two thickness levels 12.5 and 25 μm.

Detection of Cracks

The presence of discontinuities in chromium deposits was detected in chromium, plated on Hull cell test panels, by microscopic examination before and after SO_2 test. The test conditions followed the guidelines given by Edwards[11,12]. Thus, the sulfur dioxide concentration was approximately 1 per cent by vol, relative humidity was about 95 per cent, and the temperature was about 25°C. The testing was carried out in a corrosion cabinet similar to the one developed by Edwards, with the SO_2 gas, plus air, (scrubbed and humidified) passing through the cabinet continuously. According to Edwards this test is particularly suitable for the detection of discontinuities in chromium coatings and this was confirmed by detailed examination of corroded specimens under stereoscopic binocular. All dark stains, presumably due to FeS and other Fe^{++} compounds, correspond to the presence of clearly visible cracks. When the density of cracks was very high, the corrosion products would coalesce and appear to the naked eyes as droplets. If the number of cracks was very small, all corrosion products present were observed along the crack lines that could in this case be detected with the naked eye. When the coupons were plated first with nickel and then with chromium the initial attack on nickel, in the case of heavily cracked chromium deposits, was easily detected by the formation of green nickel salts. Dark brown stains did not appear until the nickel deposit was penetrated. The time required for penetration to the steel basis increased with the thickness of the nickel coatings. If the deposited nickel was stressed and cracked (from low *p*H baths) dark corrosion stains rapidly developed along the crack lines.

TABLE I

TYPES OF PLATING INTERRUPTIONS

a)	COFF1S	— current off for 1 sec
b)	COFF5S	— current off for 5 sec
c)	COFF30S	— current off for 30 sec
d)	COFF2M	— current off for 2 min
e)	W1SCON	— withdrawal of cathode for 1 sec with current on
f)	W5SCON	— withdrawal of cathode for 5 sec with current on
g)	W1MCON	— Withdrawal of cathode for 1 min with current on
h)	W1SCOFF	— withdrawal of cathode for 1 sec with current off
i)	W1MCOFF	— withdrawal of cathode for 1 min with current off
j)	RC	— reverse current pulse
k)	AN50MA	— anodic pulse at 500 A/m^2

Types of Plating Interruptions

As was mentioned in the introduction, the plating interruption to be effective must partially or completely deactivate the cathode film.

To evaluate the optimum interruption procedure 11 operational variations were examined. These are summarized in Table I. Four approaches, typified by (d)(e)(i)(j), were employed at time intervals corresponding to the deposition of the following thicknesses: 2 x 1.5 μm; 3 x 1.0 μm; 4 x 0.75 μm; 6 x 0.5 μm; and 12 x 0.25 μm to a total thickness of 3 μm in each case. The coatings obtained in this way were then tested for corrosion performance in comparison with conventional deposits plated from the same bath to the same thickness level at the same current densities and temperatures. All 11 types of interruptions were then tested at the optimum interval of time which corresponded to the deposition of 6 x 0.5 μm layers to a thickness of 3 μm.

To clarify the exact procedure used during each of the interruptions employed, they are described below in some detail:

(a) COFF1S—This procedure involved current interruption for a period of one sec by opening and closing a circuit breaking switch without otherwise disturbing the position of the specimens in the bath.

(b) COFF5S—Current interruption for a period of 5 sec in the same manner as in (a).

(c) COFF30S—Current interruption for a period of 30 sec by opening and closing circuit switch as in (a).

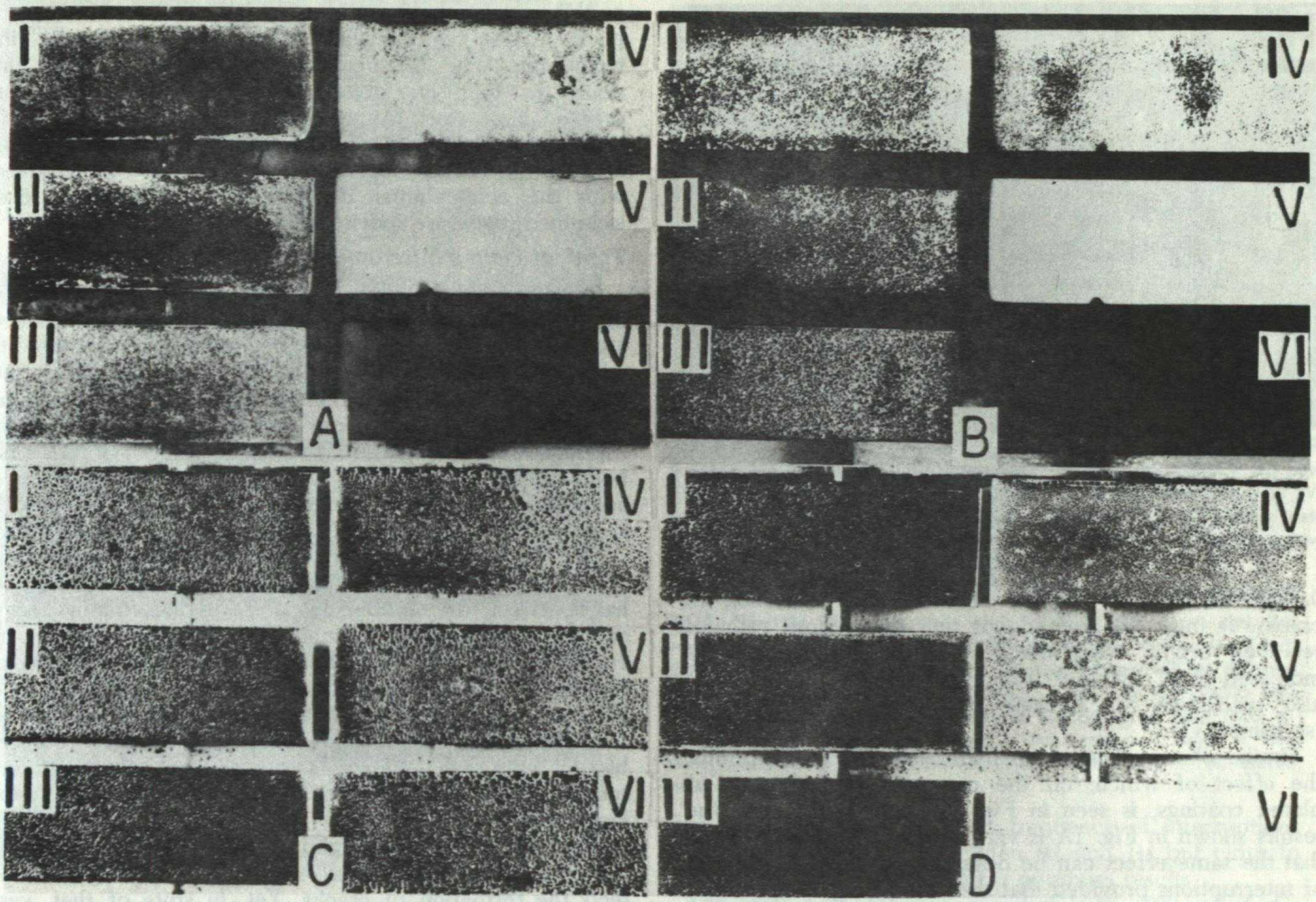

Fig. 1. Corrosion failures of 3 μm thick chromium coatings (accelerated SO_2 test) deposited with increasing number of four types of interruptions: **A.** COFF2M, **B.** RC, **C.** W1SCON, **D.** W1MCOFF. Number of interruptions: I. None, II. One, after 6 min (1.5 μm), III. Two, every 4 min (1 μm), IV. Three, every 3 min (0.75 μm), V. Five, every 2 min (0.5 μm), VI. Eleven, every min (0.25 μm). All platings at 45°C and 2200 A/m^2 on bare smooth steel from a bath containing 250 g/l of CrO_3 and 2.5 g/l of H_2SO_4.

(d) COFF2M—Current interruption for a period of 2 min as in (a).

(e) W1SCON—In this plating interruption the cathode was lifted from the plating bath until it cleared the surface of the solution. The cathode was then reintroduced into the bath after about 1 sec while the circuit breaking switch remained in the ON position throughout the operation.

(f) W5SCON—The plating was interrupted as in (e) while keeping the cathode in the air above the solution for 5 sec.

(g) W1MCON—As in (e) but extending the withdrawal time to 1 min.

(h) W1SCOFF—In this operation the current was first turned off by opening the circuit breaking switch. The cathode was then lifted up from the bath into the air and was subsequently reintroduced into the bath after about 1 sec. The circuit breaking switch was then turned on.

(i) W1MCOFF—As in (h) but the cathode remained in the air above the bath for 1 min.

(j) RC—The current circuit was rendered open, and the polarities were reversed immediately, thus making the working electrode anodic and the counter electrodes (lead anodes) cathodic for a fraction of a sec. The plating polarities were then immediately restored. The current density of the working electrode during reversal of polarities was 4400 A/m^2 (anodic).

(k) AN50MA—Working electrode was made anodic at a nominal C.D. of 500 A/m^2. In this case the plating interruption was of the same type as in (j) except that the working electrode was rendered anodic at a much lower current density. In order to accomplish such an operation an auxiliary independent d-c circuit was installed using a d-c battery and a platinum anode. The main plating current was first turned off by opening the circuit breaking switch. The low C.D. anodic circuit was then turned on for a fraction of a sec. The plating was then resumed by turning on the main (cathodic) circuit.

RESULTS

Chromium on Steel

Frequency of Plating Interruptions

For reasons of experimental expediency, the effects of only four plating interruptions, COFF2M, W1SCON, W1MCOFF and RC were examined in relation to their frequency of application.

The tests show 1) that the incidence of crack formation is markedly reduced when the frequency of plating interruptions approaches the value equivalent to the deposition of 0.5 μm thickness of chromium and 2) that the above effect varies with the type of interruptions.

These conclusions can be drawn from an inspection of Figs. 1A to 1D which represent the visual appearance of the corroded sets of specimens.

Figure 1A shows a comparison of the effect of COFF2M interruptions on the corrosion performance of 3 μm thick deposits. Specimens (I), (II) and (III) are equally heavily corroded which demonstrates that one interruption at 1.5 μm and two interruptions at 1.0 μm levels do not effectively reduce the incidence of crack formation. A marked decrease in the density of cracks is observed with specimen (IV) which was plated with three interruptions, each made at the thickness level of about 0.75 μm. Specimen (V) is completely free of any visible corrosion failures which indicates that five interruptions at

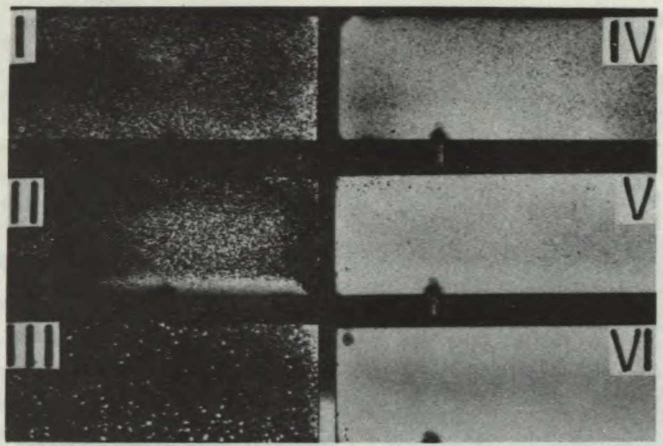

Fig. 2. Corrosion performance of conventional (I, II, III) and crack-free (IV, V, VI) coatings at the same thickness levels of 1.5 μm (I and IV), 2.5 μm (II and V) and 5.0 μm (III and VI), deposited on wet blasted steel without (I, II, III) and with RC interruptions every 2 min (0.5 μm) with specimens IV, V and VI. Other plating conditions as in Fig. 1.

0.5 μm level do effectively eliminate the formation of cracks. It must be pointed out that the deposit remains relatively bright. When the number of interruptions was increased to 11 (each at 0.25 μm level) the coating was also crack-free but became dark gray in appearance (specimen VI).

Similar observations were made with RC interruptions, the effect of which, on the corrosion performance of plated coatings, is seen in Fig. 1B. Agreement with the results shown in Fig. 1A is very exact. This demonstrates that the same effect can be obtained with different types of interruptions provided that their frequency is the same.

The selection of the correct type of interruption is important as one can infer from the inspection of Figs. 1C and 1D.

Figure 1C shows series similar to those shown in Figs. 1A and 1B, but with W1SCON interruptions. It is seen that performance-wise there is no detectable difference between all six specimens plated with interruptions spaced in the same way as in Figs. 1A and 1B. They are all as heavily corroded as the conventional deposit in specimen (I) due to high density of cracks.

Figure 1D shows the results of a series of platings similar to those shown in Figs. 1A to 1C, but with interruptions W1MCOFF. The test shows that the specimens (I), (II) and (III) are equally heavily corroded. There is considerable improvement in the case of specimens (IV) and (V), but the formation of cracks is not completely eliminated. Their density is markedly reduced and individual fissures can be detected visually. Absence of visual cracks characterizes the performance of specimen (VI) which also shows some minor deterioration of the coating's appearance.

From a practical point of view 2 min current interruption (COFF2M) is not a very suitable technique because it stretches the overall plating time excessively. The reverse current technique, on the other hand, provides very effective plating interruption since the anodic pulse lasts only for a fraction of a second.

To test the commercial feasibility of the reverse current technique with a surface preparation involving wet blasting with aluminum oxide slurry, conventional chromium coatings 1.5 μm, 2.5 μm, and 5 μm were compared with coatings plated under exactly the same conditions except for reverse current interruptions every 2 min; i.e. every time 0.5 μm of chromium was plated.

Figure 2 shows pairs of specimens corroded in the SO_2 accelerated test. On the left hand side, specimens (I), (II) and (III) were plated with conventional chromium; on the right hand side, specimens (IV), (V) and (VI) were plated to the same thickness level but with the RC interruptions. The photograph demonstrates beyond any doubt that there is a great improvement in the corrosion protection of steel by coatings deposited with the RC technique. Corrosion protection improves as the thickness of the coating increases, a feature not encountered with the conventional deposits at the thickness level examined (compare specimens I and III).

Types of Plating Interruptions

When it was definitely established that the frequency of the plating interruptions is of paramount importance and that the optimum conditions for crack-free deposits are associated with interruptions corresponding to the deposition of 0.5 μm layers, other types of interruptions at these optimum conditions were evaluated. The interruptions were compared in batches of six. In the first batch current interruptions COFF1S, COFF5S, COFF30S and COFF2M were compared directly with RC, and with a conventional deposit.

The results of the test are seen in Fig. 3A. Comparison of specimen (I) with (II) shows that a 1 -sec interruption has no effect, the number of failures being equally heavy as with a conventional coating. Extending the duration of current interruption through 5, 30 sec to 2 min markedly reduced the incidence of crack formation, but not quite as effectively as the RC technique (specimen VI).

A comparison of coatings deposited on mild steel, wet blasted with Al_2O_3 slurry, shows similar effect of current interruptions as is seen in Fig. 3A. Here the photograph in Fig. 3B does not show individual crack-lines. Apparently the initial roughness of the surface as compared with the buffed Hull cell test panels, Fig. 3A, affects the formation of cracks. Yet, in spite of that, vast improvement is achieved by using the current interruption technique.

Plating interruptions W1SCON, W5SCON, W1MCON, W1SCOFF, W1MCOFF and AN50MA were compared separately. Results of the corrosion tests are seen in Fig. 3C.

It is evident that the withdrawal of the cathode from the bath for a period of about 1 sec does not decrease the incidence of crack formation regardless of whether the interruption is made with the current on or off (specimens I and IV). Extending the withdrawal time to 5 sec decreased markedly the incidence of cracks which, at the lower crack density, could easily be individually recognized (specimen II). Further improvement resulted by extending the withdrawal time to 1 min with either the current on or off procedures (specimens III and V). A pulse of low C.D. anodic polarity applied to the working electrode for a fraction of a sec produced similar results (specimen VI).

Plating With Low C.D. and in a Concentrated Bath

At the start of the investigation it was assumed that for optimum results plating interruptions must be made at intervals of time corresponding to the deposition of about 0.5 μm of chromium.

If the crack formation is related to the incremental increases of the deposit thickness, then, at lower C.D., the spacing of the interruptions must be adjusted to account not only for the lower current rate but also for the changes in plating efficiency which varies with C.D. and temperature. Since at the C.D. of 1100 A/m^2 and the temperature of 40°C the rate of plating is about 0.1 μm/min, the plating interruptions should be spaced at 5-min intervals; that is, at plating times 2.5 times those applicable under conventional plating conditions.

Figure 4A shows four specimens tested in the usual manner in the SO_2 test. They were plated with 4.2 μm

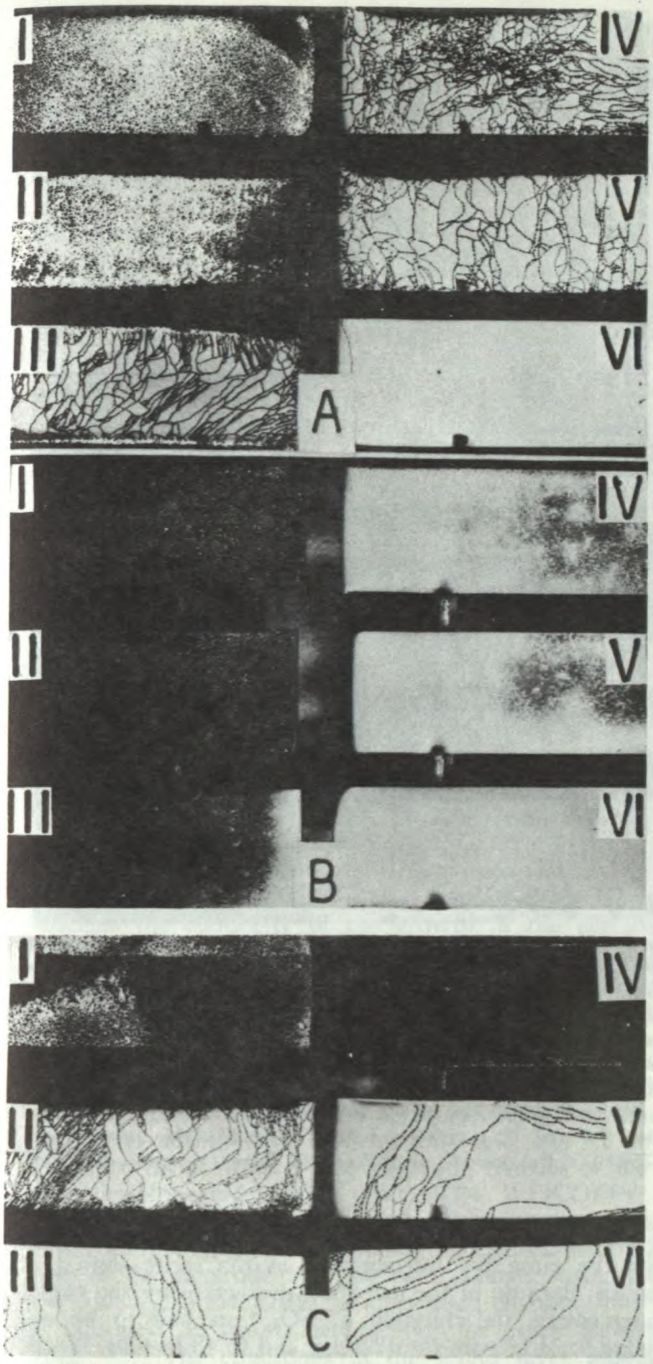

Fig. 3. Effect on the corrosion performance of different interruptions at the same frequencies (every 0.5 μm) with 3 μm deposits. **A.** Type of interruptions. I. None, II. COFF1S, III. COFF5S, IV. COFF30S, V. COFF2M, VI. RC. Other plating conditions as in Fig. 1. **B.** Type of interruptions. I. None, II. COFF1S, III. COFF5S, IV. COFF30S, V. COFF2M, VI. RC. Plating conditions as in Fig. 1 but on aluminum oxide wet blasted surface. **C.** Type of interruptions. I. W1SCON, II. W5SCON, III. W1MCON, IV. W1SCOFF, V. W1MCOFF, VI. AN50MA. Plating conditions as in Fig. 1 on smooth steel as in A.

of chromium at the C.D. of 1100 A/m^2 and a temperature of 40°C. Specimen (I) was plated continuously, that is, without interruptions. Specimen (II) was plated with the reverse current interruptions (RC) every 7 min and specimens III and IV every 5.25 and 3.5 min, respectively.

Comparison of specimens I and II suggests some improvement in performance when the plating was interrupted every time 0.7 μm of chromium was deposited. A very marked improvement is observed with specimen III in which some areas are relatively free of cracks. Complete absence of cracks is seen on specimen IV when the plating interruptions were applied every 0.35 μm of chromium. Thus, the optimum frequency of interruptions is somewhere between specimen III and IV but close to the range of 5 min predicted for optimum results.

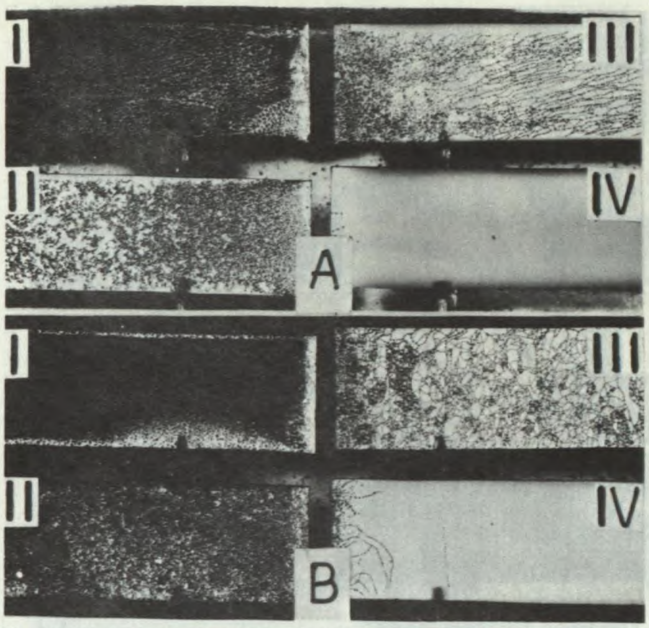

Fig. 4. Effect of RC interruptions at lower CD (1100 A/m^2) and temperature (40°C) with 4.2 and 3 μm thick deposits. **A.** Conventional bath (250 g/l of CrO_3, 2.5 g/l of H_2SO_4). Number of interruptions: I. None, II. Five every 7 min (0.7 μm), III. Seven, every 5.25 min (0.525 μm), IV. Eleven, every 3.5 min (0.35 μm). **B.** Concentrated bath (400 g/l of CrO_3, 4.0 g/l of H_2SO_4). Number of interruptions: I. None, II. Five, every 8 min (0.50 μm), III. Seven, every 6 min (0.4 μm), IV. Eleven, every 4 min (0.25 μm).

The tests with the concentrated bath (400 g/l CrO_3 and 4 g/l H_2SO_4) at the same C.D. of 1100 A/m^2 and a temperature of 40°C, show similar effect of the RC interruptions on the decrease of crack formation. However, real improvements were observed at interruptions corresponding to lower thickness of the deposited chromium, as one can infer from examination of Fig. 4B. Here, specimen (I) was plated continuously with 3 μm of chromium. Specimens (II), (III) and (IV) were plated to the same thickness with RC interruptions every 8, 6 and 4 min, respectively. Some minor improvement can be detected with specimen (II), while an unambiguous decrease of cracks is evident with specimens III and IV. Since the average plating rate under these conditions is 0.062 μm/min the spacing of interruptions corresponds to the deposition of 0.4 μm of chromium on specimen III and 0.25 μm on specimen IV. This thickness level is lower than with the standard bath, perhaps because the crack formation conditions are associated with lower incremental increases in the concentrated bath.

Loss of Lustrous Appearance

In the initial experiments which were performed with mild steel subjected to blasting with aluminum oxide slurry, the main emphasis was placed on the corrosion protection of steel by chromium coatings. No attention was paid to the surface appearance, which was satin in all instances.

Subsequent experiments with the Hull cell steel panels, which were originally prefinished to a fairly lustrous appearance, have shown that there was some loss of the lustrous appearance as the number of interruptions was increased.

The lustrous appearance of a set of specimens that were plated using W1SCON interruptions is illustrated by the mirror reflection of a Kodak developer box used for the purpose. The results are shown in Fig. 5A. This

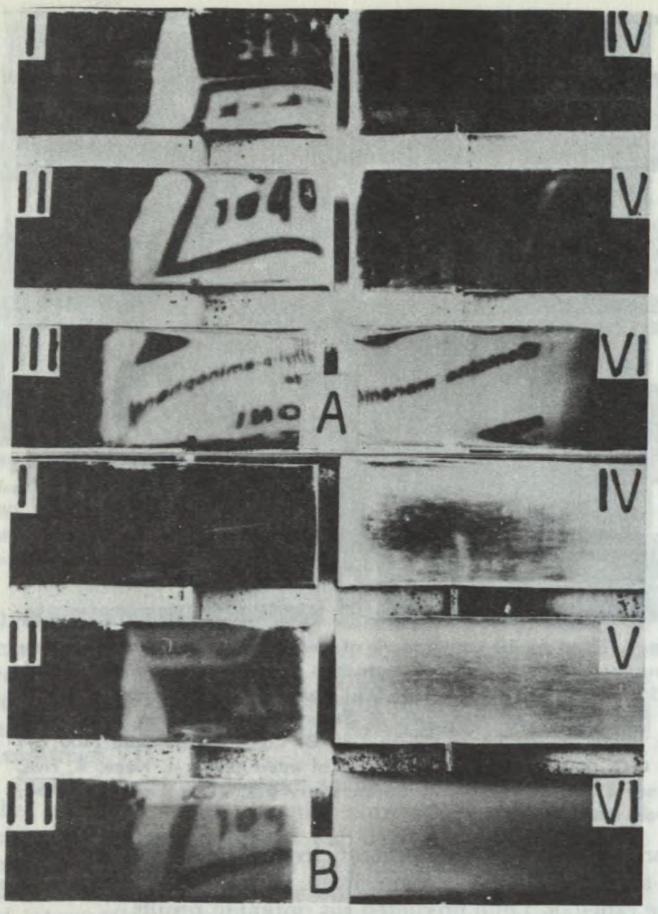

Fig. 5. Effect of interruptions on lustrous appearance of 3 μm deposits. **A.** W1SCON interruptions: I. None, II. One, after 6 min (1.5 μm), III. Two, every 4 min (1 μm), IV. Three, every 3 min (0.75 μm), V. Five, every 2 min (0.5 μm), VI. Eleven, every min (0.25 μm). Other plating conditions as in Fig. 1. **B.** W1MCOFF interruptions: I. None, II. One, after 6 min (1.5 μm), III. Two, every 4 min (1 μm), IV. Three, every 3 min (0.75 μm), V. Five, every 2 min (0.5 μm), VI. Eleven, every min (0.25 μm). Other plating conditions as above.

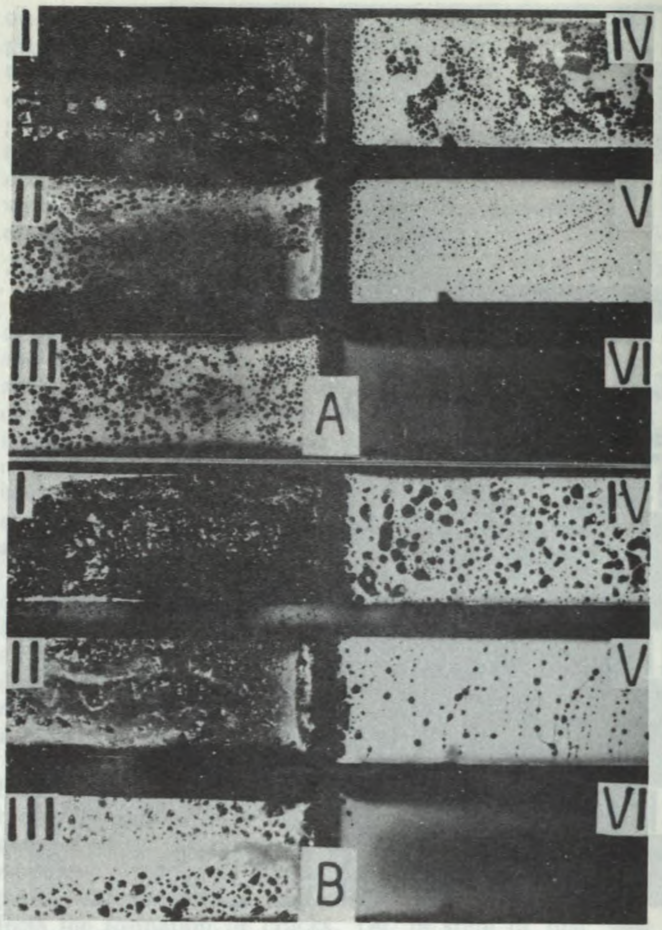

Fig. 6. Corrosion performance of cracked and crack-free chromium with 12.5 μm and 25 μm nickel undercoatings. Conventional chromium plating as in Fig. 1. RC interruptions. (For nickel plating conditions see text). **A.** 12.5 μm of nickel + 3 μm of chromium. Chromium plating interruptions: I. None, II. One, after 6 min (1.5 μm), III. Two, every 4 min (1 μm), IV. Three, every 3 min (0.75 μm), V. Five, every 2 min (0.5 μm), VI. Eleven, every min (0.25 μm). **B.** 25 μm of nickel + 3 μm of chromium. Chromium plating interruptions: I. None, II. One after 6 min (1.5 μm), III. Two, every 4 min (1 μm), IV. Three, every 3 min (0.75 μm), V. Five, every 2 min (0.5 μm), VI. Eleven, every min (0.25 μm).

series of specimens is the same that was later rephotographed after the corrosion tests and is shown in Fig. 1C. All mirror reflections were the same. Specimens IV and V in Fig. 5A look darker due to different angle of reflection.

The results show that brief plating interruptions, such as the withdrawal of the cathode from the plating bath for a period of about 1 sec, do not break up the continuity of the plating process.

When the cathode was removed from the plating solution for a period of one min, an effective interruption of the plating process was obtained and the reflectivity of the surface gradually diminished as is seen in Fig. 5B. The appearance of the specimens after the corrosion test is seen in Fig. 1D and there is some correlation between the degree of failure and the loss of reflectivity, both decreasing with the increase of plating interruptions. At the highest number of interruptions (specimen VI) the reflectivity is zero and so is the presence of detectable cracks.

Chromium on Bright Nickel Deposits

The loss of luster is a very detrimental impediment in the decorative field of chromium plating. To check whether a loss of luster occurs on bright nickel and whether a crack-free chromium provides additional corrosion protection, a restricted number of tests was made in which bright nickel was first deposited to a thickness level of 12.5 μm and 25 μm and then finished with 3 μm of chromium. The top chromium coatings were plated with the same RC interruptions as the series shown in Fig. 1B. Because of the increased protection by the nickel undercoating, the duration of SO_2 tests had to be extended to 24 hr with the 12.5 μm and to 48 hr with 25 μm nickel deposits.

The results of the tests with 12.5 μm of nickel and 3 μm of chromium are seen in Fig. 6A. As in the case of chromium on steel there is a visible overall improvement of corrosion performance when the interruptions of Cr plating decreased to 2-min intervals, which at the standard plating conditions employed corresponds to 0.5 μm thickness of chromium (specimen V). At 1-min intervals the chromium deposit became gray, thus obscuring completely the high luster characteristics of the bright nickel coating (specimen VI). The heavily cracked chromium on specimens I to III permitted an extensive attack of the corrosive medium on the nickel undercoating. The corrosion of nickel was evident through the presence of large quantities of green nickel salts on the surface of the test specimens. There were also a considerable number of dark brown stains indicating complete penetration of both protective coatings through to the steel substrate (specimens I to IV). With specimen V such penetration was minimal and none was observed with specimen VI.

The results of a SO_2 test with 25 μm of nickel and 3 μm of chromium are seen in Fig. 6B. As in the case of the thinner nickel deposit, the improvement of corrosion performance with the increased number of interruptions of chromium plating is quite evident. The attack on nickel through the pores in the cracked chromium (specimens I, II and III) was of similar intensity. Penetration to the basis metal was almost nil which indicates increased protection by thicker nickel deposits. Some penetration to the steel substrate occurred with specimens IV and V, while there was an unambiguous decrease of visible green nickel salts. Apparently, as the number of cracks in the chromium decreased, the attack on the nickel intensified in depth at the reduced number of pores, thus increasing the rate of penetration through the nickel coating. When the chromium became completely pore-free (specimen VI) there was no evidence of any attack on the nickel (no green nickel salts or any penetration through to the steel substrate (no dark-brown stains).

As in the case of buffed steel, there was a loss of the overall result was less severe because of higher initial luster of the nickel undercoating.

DISCUSSION

Significance of Plating Interruptions

Study of the experimental results clearly shows that effective interruptions of the chromium plating process reduce the incidence of crack formation and the lustrous appearance of the deposit. Simple interruptions of the process (COFF1S, W1SCON, W1SCOFF) do not affect the formation of cracks or the appearance of the deposit. Apparently, an interruption is effective only when it disrupts the continuity of the growth of the chromium plate. The growth continuity is disrupted with longer current interruptions (Fig. 3A) which indicates the need for dissipation of the plating conditions in the liquid layer adjoining the cathode surface. These conditions do not dissipate even when the cathode is withdrawn completely from the bath for a brief period of time (Fig. 3C), which suggests that the liquid layer adjoining the cathode surface is adsorbed at the electrode and can be lifted out from the solution. If the electrode remains in the air for a brief period of time (W1SCON, W1SCOFF), the changes in the liquid layer are not drastic enough to affect the continuity of the plating process on reintroduction of the electrode into the bath. Longer withdrawals (W1MCON, W1MCOFF) produce such changes, and this is indicated by lower incidence of the crack formation (Fig. 3C). The conditions in the liquid layer adjoining the cathode surface are drastically altered by a brief anodic pulse at high or low current densities (RC, AN50MA) (Figs. 3A and 3C).

All the above observations can be plausibly explained by assuming the existence of an adsorbed cathode film. The formation of such a film prior to the beginning of chromium deposition has been discussed in earlier reports[8,9]. Its existence is essential for the process $Cr^{6+} \rightarrow Cr^{\circ}$ to continue. Any plating technique that will cause deactivation or destruction of the adsorbed cathode film will effectively interrupt the plating process. Partial dissipation of the film, for instance, during COFF5S, COFF30S, COFF2M does not produce as effective a plating interruption as RC, presumably because dissipation of the film by simple dissolution is a slow process compared to dissipation produced by an anodic pulse. The effectiveness of the anodic pulse is consistent with the dependence of the film's existence on the more negative potentials. Anodic pulses which shift the electrode potential toward noble (more positive) values either deactivate or destroy the nature of the film. Thus, on resumption of the cathodic polarity the film must be re-established and re-adsorbed, following which the deposition of chromium is re-initiated. The method of withdrawal of the cathode from the plating bath is similar in principle to the current interruptions except that when the withdrawal is made for longer periods of time (W1MCON, W1MCOFF) the constituents of the film adhering to the surface are not diluted by the plating solution. Thus, on introduction into the bath the re-establishment of the cathode film is facilitated by their presence, and the interruption is not quite as effective (compare Figs. 1A and 1D).

Frequency of Plating Interruptions

Plating interruptions effectively reduce the formation of cracks if they are applied with sufficient frequency to prevent the incremental increase of the deposit thickness which, under conventional plating conditions, is related to deposition of chromium < 0.75 μm thick. This principle is experimentally demonstrated in Figs. 1A and 1B. Figures 1C and 1D show that the principle is not workable if the plating interruptions are not fully effective.

With an effective interruption, such as RC, the absence of cracks was observed to be related to the deposition of 0.5 μm of chromium, which under the conventional plating operation (C.D. 2200 A/m^2, temp 45°C) required 2 min of electrolysis. At lower C.D. (1100 A/m^2) and lower temperature (40°C), when the plating rate is much lower, the optimum frequency of interruptions was every 5 min, which also corresponds to the deposition of 0.5 μm of chromium.

Plating interruptions more frequent than the above optimum will also produce crack-free deposits but their appearance deteriorates rapidly as the number of the interruptions increases.

It is obvious from the foregoing that modification of the current flow involving plating interruptions will produce partially or totally crack-free chromium. This principle is the basis of many reports or patents which claim improvements of chromium coatings within some very narrow ranges of empirical data[13-20].

Using the technique described, thick (up to 25 μm) crack-free coatings have been plated employing RC interruptions every 0.5 μm. The spacing of interruptions does not have to be precisely every 0.5 μm. Coatings with substantially reduced cracks were produced by using alternative spacings of 0.5 and 0.75 μm. It is important, however, to remember that some cracks may form at 0.6 μm level and interruption every 0.75 μm thickness will not eliminate them. Thus we observe for instance an interesting phenomenon of zoning in Fig. 1D where there are areas free of cracks and separate distinct areas heavily cracked. A similar phenomenon is also seen distinctly in specimen III Fig. 4B, plated with interruptions spaced somewhat more closely. Apparently, in concentrated baths the critical thickness at which formation of cracks occurs is somewhat lower than in the standard bath, and adjustment in this respect is necessary.

Question of Stresses, Layers, Current Efficiency and Throwing Power

A major concern regarding the interrupted method of chromium deposition is whether such coatings develop latent stresses that would eventually bring about delayed fractures. The answer to this question is that we do not know for sure. Examination of 12.5 μm thick coatings plated with RC interruptions every 0.5 μm did not reveal the presence of any cracks after 6 months of aging at room temperature. These observations, however, were not considered conclusive.

One can speculate that since 0.5 μm thick chromium deposits remain crack-free even though they are somewhat stressed[4], thick coatings built up with 0.5 μm units will be stressed to the same extent only, because they are not cracked. In other words one can assume that the stresses in thicker interrupted coatings are not cumulative and that the formation of cracks is avoided for the same reason as in the 0.5 μm thick units.

The above line of reasoning must, however, remain highly speculative in the absence of experimental stress data measurements.

Another question which is of considerable concern is whether the interrupted procedure produces distinct layers of chromium, and if it does, whether their adherence is sufficient to meet the requirements of practical utilization.

Plating interruptions generally lead to banded structures[6]. Banded structures are also observed in conventional deposits plated continuously[6,7,21]. Doss[22] has found that the effect of plating interruptions on the formation of distinctly visible (in cross sections) layers is selective. He found, for instance, that removal of the plated parts from the plating solution for 1-min intervals, and regulating the temperature alternatively between 51°C and 59°C produced visible laminations. Interruption of current for 1 min and reversing the current for 15 sec did not produce distinct layers although, as is reported in the present work, this type of interruptions reduces or eliminates the incidence of crack formation. His work has also shown that adhesion problems do not normally occur in coatings of this type.

Current efficiency and throwing power were not expected, at the outset, to be affected by plating interruptions, since essentially they must be the same as those observed during plating of 0.5 μm thick deposits. This was confirmed experimentally. All deposits, whether they were plated continuously or with interruptions, had thicknesses that corresponded directly to the total actual plating time. However, it is obvious that if 2 min interruptions were used, the process time was extended by this idle period. There were no significant idle periods with RC interruptions, the reversal of the current lasting only fraction of a sec. There was also no measurable decrease of the plating rate which would be expected if the reverse current was kept flowing for any significant period of time, due to an anodic dissolution process which takes place under these conditions.

Throwing power also appeared to be unaffected by the interruption technique used to plate crack-free chromium on the inside rims of a 7 mm hole punched in the center of the test specimens.

To all intents and purposes, all the advantages of conventional chromium plating, with the exception of macro-lustrous appearance, were observed to be maintained when depositing crack-free chromium by the interruption technique described.

CONCLUSIONS

1. Conventional chromium plating bath (CrO_3 250 g/l, H_2SO_4 2.5 g/l) yields crack-free deposits in the bright chromium plating range (for instance at C.D. 2200 A/m^2, temp. 45°C) when the progress of plating is interrupted at intervals of time corresponding to the deposition of 0.5 μm of chromium.

2. When the interruptions are more frequent, corresponding to the deposition of 0.25 μm of chromium, the coatings remain crack-free but become dark grey.

3. When the interruptions are less frequent, corresponding to the deposition of 0.75 μm of chromium, the coatings are more lustrous in appearance but are only partially freed from the presence of cracks.

4. At low C.D. of 1100 A/m^2 and a temperature of 40°C, interruptions spaced at about every 0.5 μm of chromium were found to suppress the formation of cracks in a conventional bath (CrO_3 250 g/l, H_2SO_4 2.5 g/l). In a more concentrated bath (CrO_3 400 g/l, H_2SO_4 4 g/l) interruptions every 0.25 μm of deposited chromium were required to completely eliminate the presence of cracks.

5. Within the limited range of plating conditions examined, such variables as current density, bath temperature and composition were found not to have significant effect on the process of crack reduction through the technique of controlled plating interruptions.

6. Different types of interruptions with ability to break up or deactivate the cathode film were found applicable, provided they were employed with sufficient frequency to prevent the periodic formation of cracks. Optimum interruptions tested were anodic pulses at high (4400 A/m^2) and low (500 A/m^2) current densities.

7. Anodic pulses applied through the employment of reverse current techniques permit crack-free chromium to be plated at practically the same plating speeds as a continuous deposition process. The technique does not require a) special equipment, b) new bath formulation and c) rigid control of current density, temperature or frequency of interruptions, provided that the thickness of chromium associated with one cycle of crack formation is not exceeded. The crack-free deposits lose some lustrous appearance with increased number of interruptions, but remain mirror bright on the microscale when the frequency of interruptions is not too high.

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