R&D 5686-MS-01

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ELECTRODEPOSITION OF DENSE CHROMIUM COATINGS FROM MOLTEN SALT ELECTROLYTES

Final Technical Report

by

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April 1991

United States Army
European Research Office of the U.S. Army
London, England

Contract Numbert DAJA 45-87-C-0047
Contractor C.N.R.S.

Approved for Public Release : distribution unlimited

Abstract :

- Our research has showed the feasibility by pulsed current of chromium plating on nickel, iron, 4340 alloy. All the samples had a flat surface.

- The morphology of the deposits were examined by electronic microscopy. All the observations confirm :

. the compacity of the coatings with a uniformity in size of cristals.

. the good continuity between the deposit and the matrix.

. the grain size and the preferential orientation in the growth after etching of a cross section.

- All the trials to obtain a coating inside a nickel or 4340 alloy cylinder were always a complet check.

Keywords

Chromium, coatings, molten salts, pulsed currents, electrodeposition.

The results, on the electrodeposition of dense chromium coatings from molten salt electrolytes, obtained in the previous investigations allowed to give the chemical and electrochemical conditions to apply for achieving compact, smooth and adhering coatings on matrix made of various materials.

In the first, second and third periodic report, we described the thermodynamic study of chromium salts dissolved in molten salts using the cell :

$Cl_2/C//Cr^{2+}$ in LiCl-KCl//Cr metal

The chromium ions are introduced by anodizing a piece of chromium and the concentration ranging from $C_{Cr^{2+}} = 5.10^{-3}$ to $C_{Cr^{2+}} = 0,25$ moles per litre were used.

The results show :

- that the e.m.f. E varies linearly with the temperature.
- the concentration dependence of the e.m.f. is

$$E = E^\circ - \frac{RT}{nF} \log a_{Cr^{2+}} \text{ with } a_{Cr^{2+}} = \gamma C_{Cr^{2+}}$$

γ being the activity coefficient of chromium ions and that it varies with the concentration $\log \gamma = \beta_1 C^2_{Cr^{2+}} + \beta_2 C^2_{Cr^{2+}}$

β_1 et β_2 are function of the temperature $\beta_1 = A_1 + B_1/T$;

$\beta_2 = A_2 + B_2/T$

From the e.m.f. measurements several thermodynamic values have been obtained

$$\Delta H = -363286 + 5566{,}4\, C_{Cr^{2+}} - 17142\, C^2_{Cr^{2+}}$$

The study of the deposition mechanism of chromium by voltametry and chronopotentiometry shows that the discharge reaction of chromium is a quasi reversible reaction controlled after a prolonged period of time by the diffusion of chromium ions and for short periods of time it is dependent upon the kinetics of electron transfer. Our chronopotentiometric experiments have shown that a large adsorption of chromium ions occured, the superficial concentration Γ of the adsorbed chromium ions were of $1,6.10^{-8}$ moles. cm^{-2}.

On the basis of the above findings we have examined the possibility of obtaining compact and adhering chromium coatings at temperatures below 550°C.

The concentration in chromium ions was obtained with introduction of $CrCl_3$ to provide a $CrCl_3$ concentration of one weight pourcent in three electrolytic baths

$BaCl_2$ - $CaCl_2$ - NaCl

$BaCl_2$ - KCl - LiCl

$AlCl_3$ - KCl

Refining and pulsed deposits were realised in these baths with different current densities (17-12-1 A/dm^2). From these results, we have examined in the next phase of this research

- the nuclei formation and growth mechanisms of the deposits

- the formation of deposits with pulsed currents having much shorter reduction time ($\frac{1}{100}$ to $\frac{1}{1000}$ of a second)

- the effect of an increased anodic current during the relaxation period.

The investigation of the electrocrystallization of chromium was realised by two electrochemical methods : chronopotentiometry and chronoamperometry. Based on the results of this study chromium coatings were made using pulsed current . The shape of the pulses was such that a very short pre-pulse (in the order of a millisecond) of a relatively high current amounting up to several amperes per cm^2, was applied to generate a great number of nuclei. The current is then maintened to promote the growth of these nuclei. The microscopic observations of the coatings realised on nickel and alloy 4340 confirms the good continuity between the deposit and the matrix and this explains the good adhesion of deposits.

As shown by the previous results the quality of the chromium coatings depends strongly on the properties of the ionic solutions of chromium salts and the electrochemical parameters. In order to better control the electrodeposition process we developed techniques to determine the amounts of Cr^{2+} and Cr^{3+} present in the bath. This analysis has been correlated with the thermodynamic properties of the chromium solutions (standard potential) and with the diffusion coefficients of chromium ions. After having determined the conditions for preparing the coatings the investigation has been continued to examine the qualities and properties of the coatings and to see if it were possible to reproduce easily these coatings with the same properties (Fourth interim report). To this aim many different conditions were tested to realise chromium coating on metals and alloys. The coating quality was checked to compare the morphology and the interfaces, to know if the adherence will be good or not. As it is possible to reproduce the chromium coatings with the same qualities we have extended our research to examine the influence of the sample's size on the quality of the coatings always obtained in the same conditions. Up to here the coatings were systematically realized on cathode made with differents metals and alloys (Ni, Fe, 4340 alloys...) having the shape of 1 mm thick sheet centred between the two flat anodes that were 50 mm apart.

It was interesting to show the modifications of the coating's morphology when the sample had

-3 to 5 mm thick

- an area larger than 1 cm^2

To determine the effect of the tickness and the size on the structure of the layers deposited on different materials we have studied the evolution of the coating with different electrolysis conditions. The properties were characterized by the evolution of :

- the hardness
- the grain size distribution in the chromium layer
- the prefered growth orientation
- the X ray analysis

The quality of the coatings and the interface aspect depending on the electrochemical reactions occuring during the coatings formation we tried to characterize the mechanism fo the reduction reaction by measuring the impedance of the system as a function of the imposed potential.

From all these results, it seems, that the main difficulty proceeds :

- of the presence of preferred orientation in the growth
- of a dendritic growth on the edges when the cathode area is large compared to anodic surface.

The coatings deposited on flat samples put between two anodes are realised in very favorable conditions because the convection currents help to maintain a homogeneous bath composition and the concentration is uniform and stable.

Knowing the conditions to realize good coatings on flat samples with more or less large surface we have applied this technic to perform a coating inside tubes of different diameters and lengths.

To realize this project the first problem to resolve has not an electrochemical or chemical origin but only a technological one. This difficulty is not surprising because a similar problems appears for preparing a coating inside a tube by electrolysis in aqueous solutions and we hnow the numerous and necessary conditions to adopt for obtaining a uniform and compact coating. In addition it was very difficult to adapt rapidly a solution for the deposition of refractory metals in molten salts. The first and important problem, to realize an internal coating, was to place the anode near the axis of the tube and to maintain the same distance between the anode and the internal face of the tube. It was necessary to realize this disposition between the electrodes in assuming their electric insulation.

As in aqueous medium it is not possible in molten salt to varnish the external surface of the tube to prevent a coating on this part. To minimize this effect but without varnish we thought that this external coating shoud not be realized if the volume of salt surrounding the external surface of the sample was small important.

With the system to maintain the sample in the bath and to obtain a fixed position of the anode using pyrex guides as shown in Fig. 1 we thought that the convection curent should permit a constant composition of the bath only inside the tube between the anode and the cathode but not arround the tube where the chromium ions concentration is always very low.

The first approach of the internal disposition in the cell adopted for obtaining our first coating, has shown that this conception does not permit the realization of a homogeneous coating.

In spite of all the numerous trials, realised with the electrochemical conditions giving very fine coatings on flat samples, it has not been possible to obtain a uniform and adherent coating inside some cylinder in nickel and 4340 alloys.

This complete check can be explained by the too small anodic surface of the chromium rod obtained by high frequence smelting .

It vould be useful to verifing this hypothesis and to approach better conditions, in substituting this massive anode by a cylinder of nickel wire gauze filled up of chromium chips.

Another reason which can also explain these results is the much too low current density which was limited by the potentiostat adapted for electrochemical studies and not for this production of coatings on large surfaces.

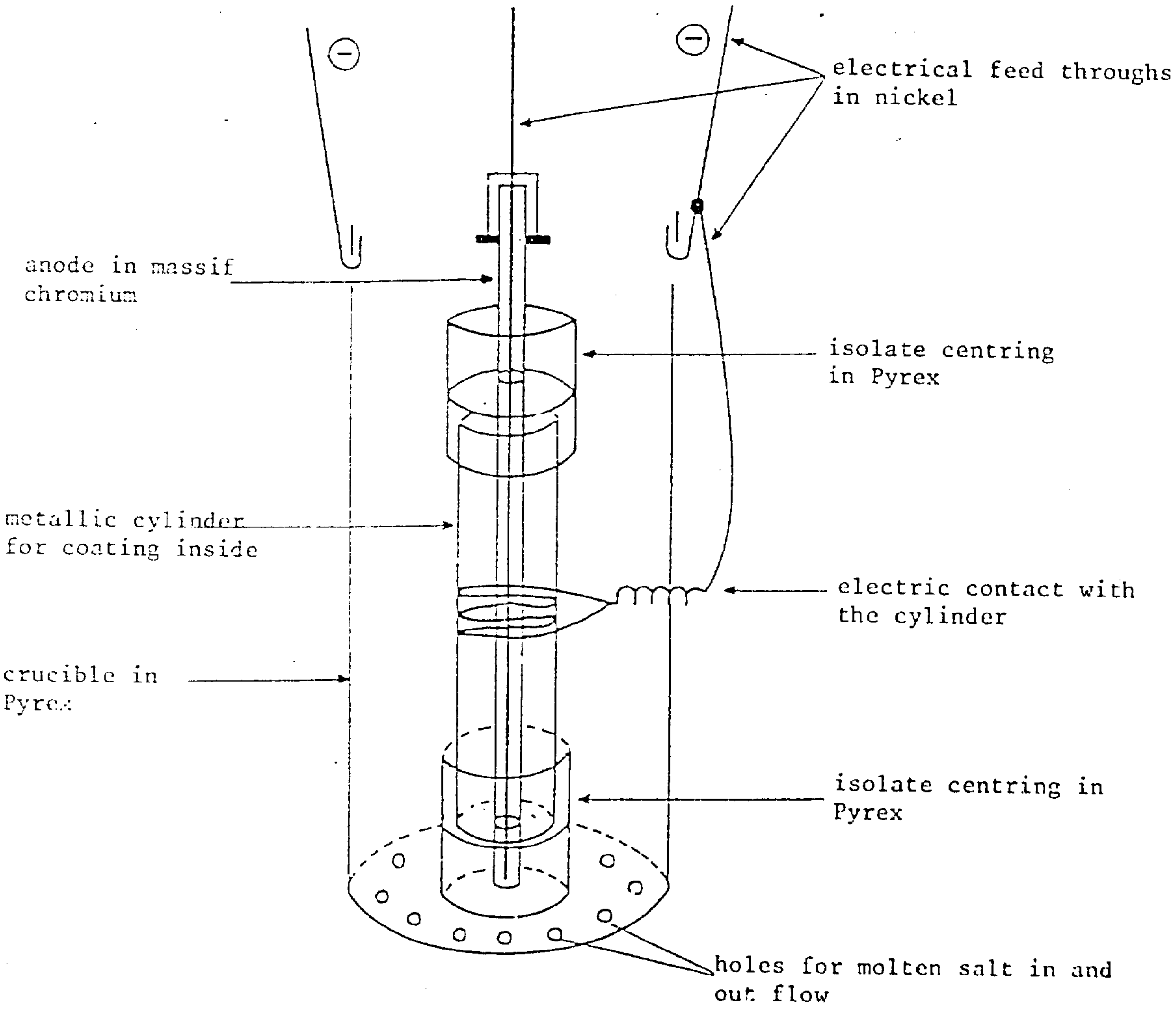

Fig 1. Moving basket either immerged in the electrolyte or lifted out.