Some Aspects of Recent Development on Functional Trivalent Chromium Plating

Patrick Benaben
Surface Treatment Laboratory – Ecole Nationale Supérieure des Mines
42023 – Saint-Etienne Cedex 2 – France
E-mail : benaben@emse.fr *– Fax : +33 4 77 42 00 00*

Abstract :

A general review of what is currently (to our knowledge) under development at a laboratory or at a pilot scale level in different countries will be discussed. As examples, we will present some formulations and results get by these different methods. We will develop also results that we get by using aqueous solutions of trivalent chromium salts obtained by careful reduction of hexavalent chromium compounds .

Application in the laboratory to deposition of composite deposits (inclusion of hard and self - lubricating particles) and Cr-Ni multilayers (application to G.M.R.) of trivalent chromium solutions will be discussed.

In conclusion, we will discuss the future of trivalent chromium processes as complementary process for hard chromium plating, using hexavalent chromium solutions. In particular we will present results on the influence of heat treatment on the hardness improvment (1600-1800 HV_{100g} – 300°C, 15 min) and we will discuss results of studies by X-Ray diffractometry on structural modifications.

I – General aspects :

Since some years, decorative trivalent chromium processes are developed through worldwide and deposits are actually indistinguishable in color from hexavalent deposits (1-2).
However, until now, there is no process to obtain at an industrial scale hard thick chromium deposit through an aqueous trivalent chromium solution.

The different reasons enumerated in literature to explain the lack of success are :

- the high potential of Cr^{3+} reduction to metallic state (-0.744 V/NHE) which explain in all cases the high hydrogen evolution at the cathode,
- the stability of the hexa-coordinated (bipyramidal shaped) aqueous trivalent chromium complex. The exchange kinetics of water molecules from Cr^{3+} complex has been evaluated and checked as 11 orders of magnitude weaker than for nickel complexes (3)
- chromium hydroxydes quickly precipitate and this phenomenon increases as the cathode pH increases with the important hydrogen evolution. .

II – Different classes of process :

Currently, two classes of processes are developed to overcome the moderate success in hard thick trivalent chromium deposition :

☛ processes using complexing agent to complex trivalent chromium ions in aqueous solution : the processes are used in decorative applications. The complexation objectives are :

  - to obtain lower potential reduction of Cr^{3+} to metallic state
  - to prevent the formation of hexa-aquo coordinated trivalent chromium complexes,

☛ processes using chemical reduction of hexavalent chromium to trivalent chromium by SO2 or alcohol, to obtain trivalent chromium ions not engaged in very stable complexes.

1 – Process using complexing agents :

These processes are used in decorative trivalent chromium applications.
Composition of the bath are given in details (4, 5, 6, 7, 8, 9, 10) and a synthesis was made in a recent publication (11)
As general indications :
These baths are using complexing agent as formate, thiocyanate or hypophosphite with in some cases additives as : glycolic acid, citrates, sulfamates.
For each of these compositions the condition of deposition such as deposition rate, throwing and covering power, microhardness, texture…etc…are very different.
In general, these deposits have a microhardness of about 700 HV_{100}, a cathodic efficiency lower than hexavalent chromium processes and so a very slow rate of deposition (0.2 0.4µm/min.).
However the covering power, cathodic current density zone in which fair metallic chromium deposition takes place, is more important for those processes than for hexavalent. This high covering power (about the same as classic nickel bath) allows to have a better coverage for parts and so allows to increase the number of parts on racks.

2 – Processes using trivalent salts obtained by reduction of hexavalent chromium ions :

☛ Reduction by SO2

The first application (12) was done in 1946 by the U.S. Bureau of Mines (USA). This process allows to prepare chromium metal by electrolytic deposition with anodic and cathodic compartment separation.

☛ Reduction by alcohol :

The process allows deposition with high efficiency (up to 30%), deposits have a microhardness of about 1000 HV_{100}, the throwing and covering power are lower than other processes. However these processes are interesting by the high rate of deposition.

The bath obtained by the methanol reduction method is developed in our laboratory (13).

This process is dangerous and hazardous, due to the high exothermic reaction of hexavalent chromium reduction by alcohol.

3 – Some particular processes :

Recently some interesting works have been developed on the influence of the current shape on the deposit of chromium through trivalent solutions.

Results are depending on the shape of the cathodic current : the influence of the first layer and the interface between cathode and solution is clearly demonstrated (14).

Also some particular applications have been disclosed for brush plating which allows to deposit chromium layer on substrate using mobile systems (15). This application could be of a major interest in the future to repair "in situ" some default in chromium layers after wear or abrasion, or on default on chromium layer after deposition.

III – Special development using trivalent chromium solution obtained by reduction:

The process developped using reduction of chromic acid by methanol alcohol in chlorhydric acid medium allows to get deposit at a rate of deposition of 3µm/min. at 80 A/dm². The process has been described and the conditions and characteristics of deposit disclosed (13).

Using this type of bath we have developed some improvement or modification of the deposit in particular in the field of deposition of multilayers and composite deposit (inclusion of Al_2O_3 particles)

1 – Cr-Ni multilayers :

The conditions and the results of research works done on Cr-Ni multilayers deposits have been presented in recent publications (16 – 17), but we present some aspects of results that we get by the single bath method using the trivalent chromium solution developped in the laboratory.

In particular fig 1 and 2 present SEM photographies of a multilayer Cr-Ni deposit with sublayer of about 0.1 to 0.2 µm on a first layer of Nickel (about 10 µm - on the substrate), and figures 3 and 4 present an AFM examination of the surface of a cross section of the multilayer deposit : due to the difference between the hardness of Cr and Ni, each waves represent in the high part the harder deposit (chromium layer) and the low part the softer deposit (nickel layer).

This AFM examination allows to evaluate the size of each layer.

The final objectives for an application in the field of micro-electronics systems is to get GMR phenomenon (important variation of electric resistance in function of magnetic field applied). This phenomenon will be only present if the thickness of each sublayer (Cr and Ni) is in the range of 0.1 nm (about 10 Angströms).

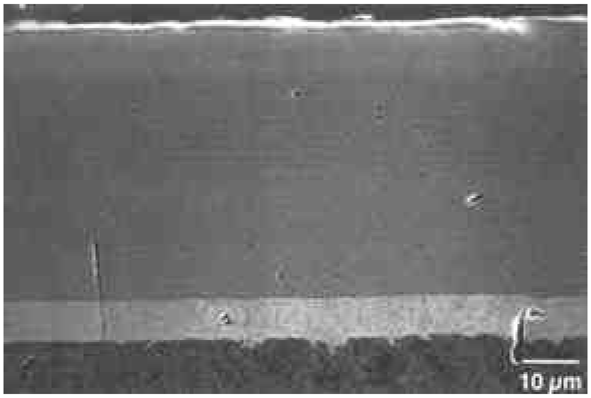

Fig. 1: SEM photo of a Cr-Ni multilayer

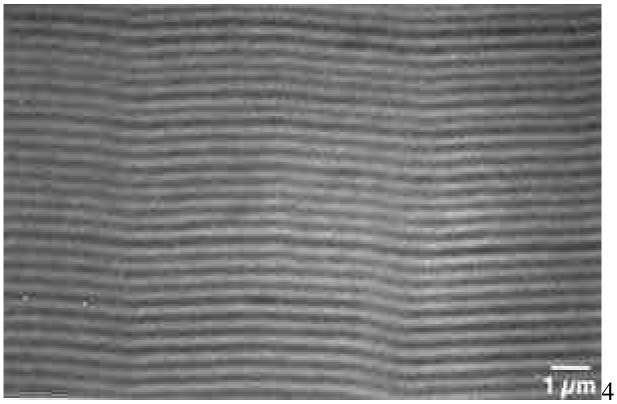

Fig. 2: SEM examination showing different layers (Cr black and Ni white)

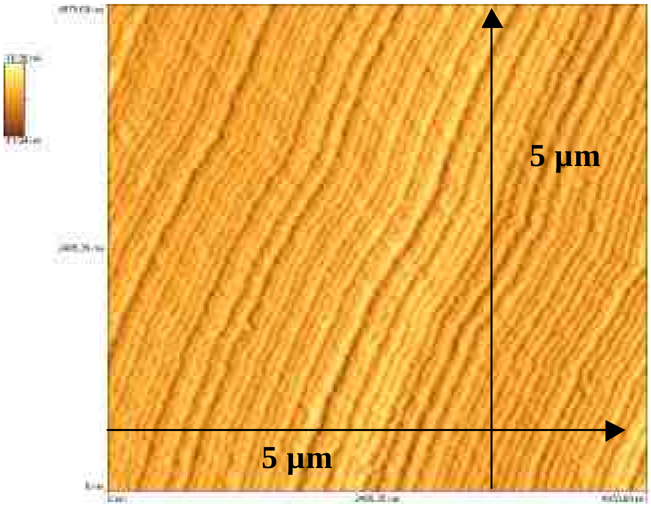

Fig. 3: AFM examination of a Cr-Ni multilayers deposit
This examination has been done on a cross section.

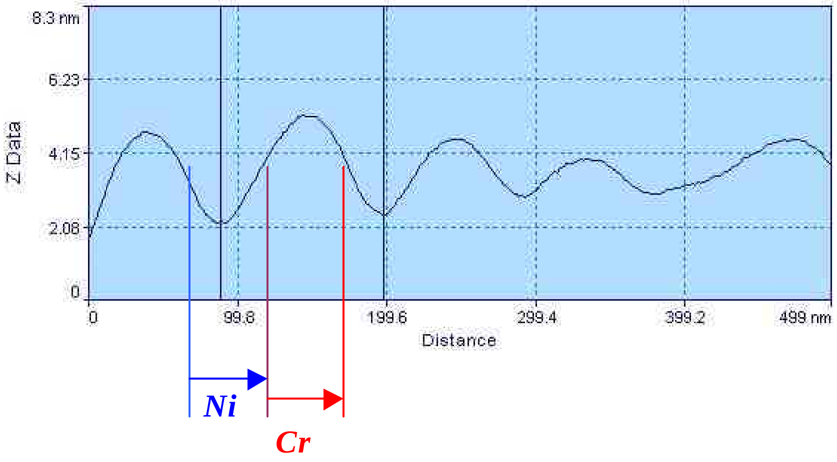

Fig. 4: Aspects of the surface (cross section) of the multilayer deposit

2 – Cr composite deposits :

About composite deposit, we present in figures 5 to 8 results get by electrodeposition of chromium from a trivalent chromium bath developped in the laboratory with Al_2O_3 particles: size between 0.3 and 2 µm. The process has been patented recently (18).

The figures present different deposits with different concentration of particles in the chromium deposit : the concentration of Al_2O_3 particles in the deposit depends on the concentration of particles in the bath.

We present in the figure 9 the variation of the concentration in the deposit function of concentration in the bath. It is interesting to note that between 10 to 20 g/l the particle concentration of the deposit does not vary in an important manner. This is of great importance in the case of composite deposits

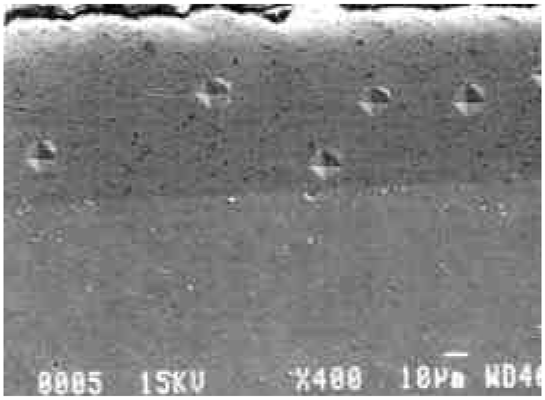

Fig. 5: Cr Composite deposit (Bath conc. 2g/l)
Particles : Al_2O_3 - 0.3 to 2 µm

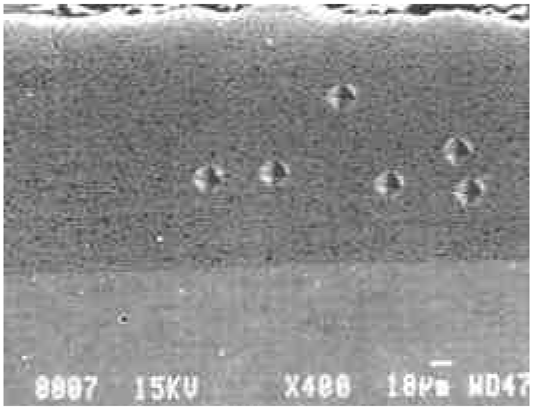

Fig. 6: Cr Composite deposit (Bath conc. 4g/l)
Particles : Al_2O_3 - 0.3 to 2 µm

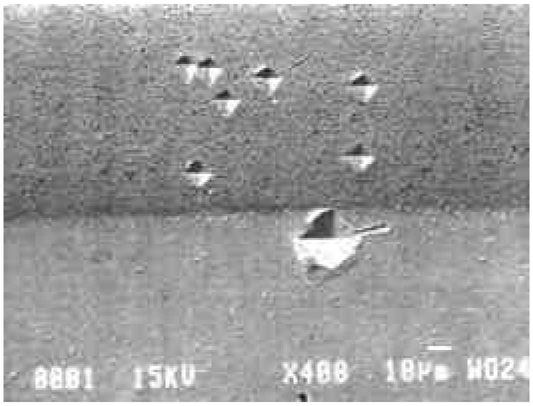

Fig. 7: Cr Composite deposit (Bath conc. 10g/l)
Particles : Al_2O_3 - 0.3 to 2 µm

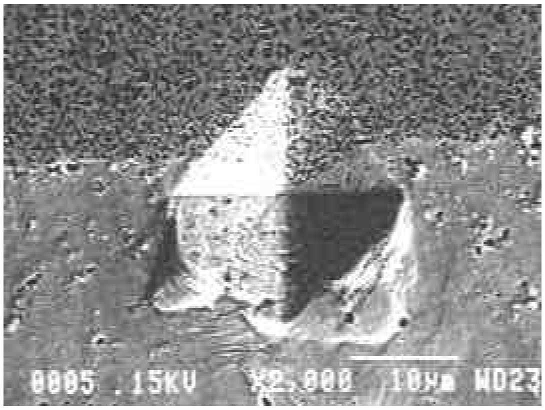

Fig. 8: Cr Composite deposit (Bath conc. 20g/l)
Particles : Al_2O_3 - 0.3 to 2 µm

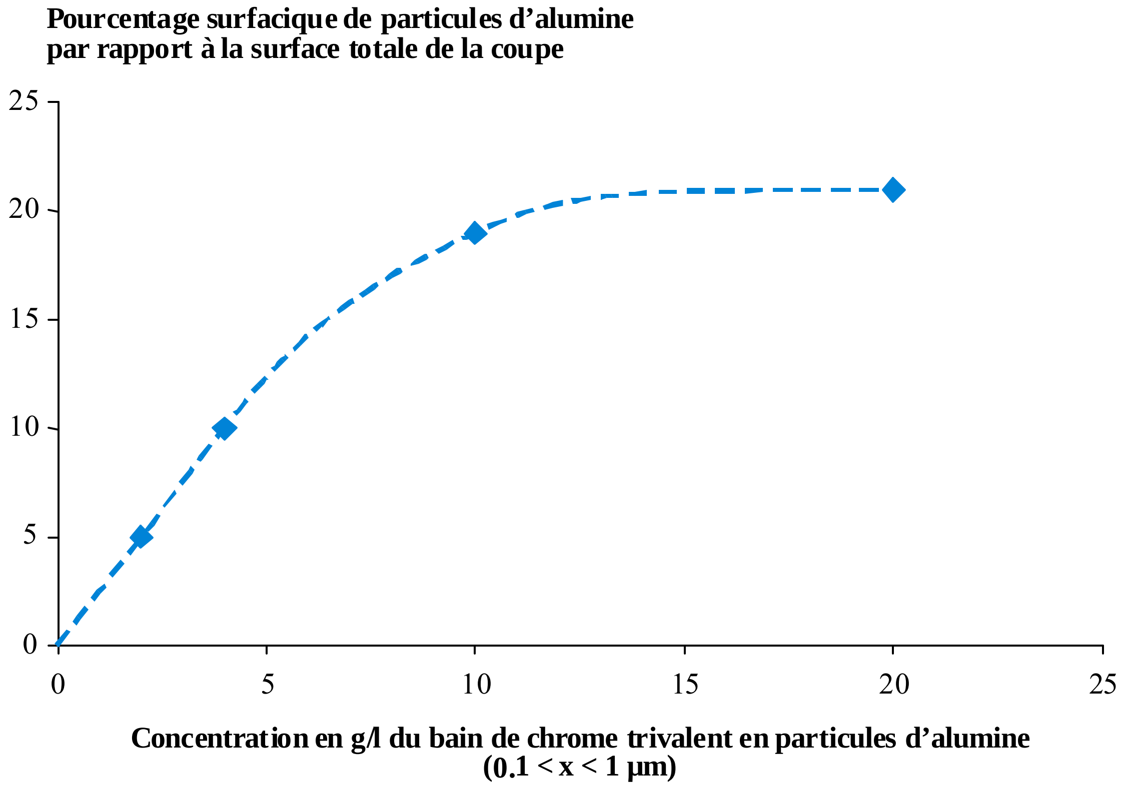

Fig. 9: Variation of concentration (in surface) of the deposit as a function of the Al_2O_3 particles concentration in the trivalent chromium bath.

IV – Influence of Thermal Treatment

Some authors already have published information about the increasing of hardness in the case of trivalent chromium deposits by heat treatment (4-8-10). We have developed in a study sponsored by AESF (19) and in a more recent paper (20) the influence of trivalent chromium hardening by thermal treatment. We have shown that, due to Cr_7C_3 and Cr_2O_3 formation during heat treatment, the microhardness is increased up to about 1700-1800 HV_{100} for a treatment: temperature 300-350 °C and duration 30 minutes and in the same time the microhardness of hexavalent chromium deposits decreased (cf. fig). We have shown (21) also that the wear resistance of trivalent chromium deposit is increased by 5 to 6 fold after heat treatment compare to hexavalent chromium deposit without heat treatment.. However due to cracks through the deposit, corrosion resistance is lower than for hexavalent chromium deposits.

In particular it has been described through structural RX examination that as soon as the temperature reaches 290-300°C, it appears that a structural modification takes place and that there is a precipitation of chromium carbide: the chromium carbides formed prevents the dislocations to move and so an increase of hardness occurs.

We present in figure 10 variation of microhardness as a function of temperature for trivalent and hexavalent chromium deposits. It appears clearly that the variation is fundamentally distincts and in the case of trivalent chromium deposits, the variation is similar to variation of microhardness vs temperature for electroless nickel.

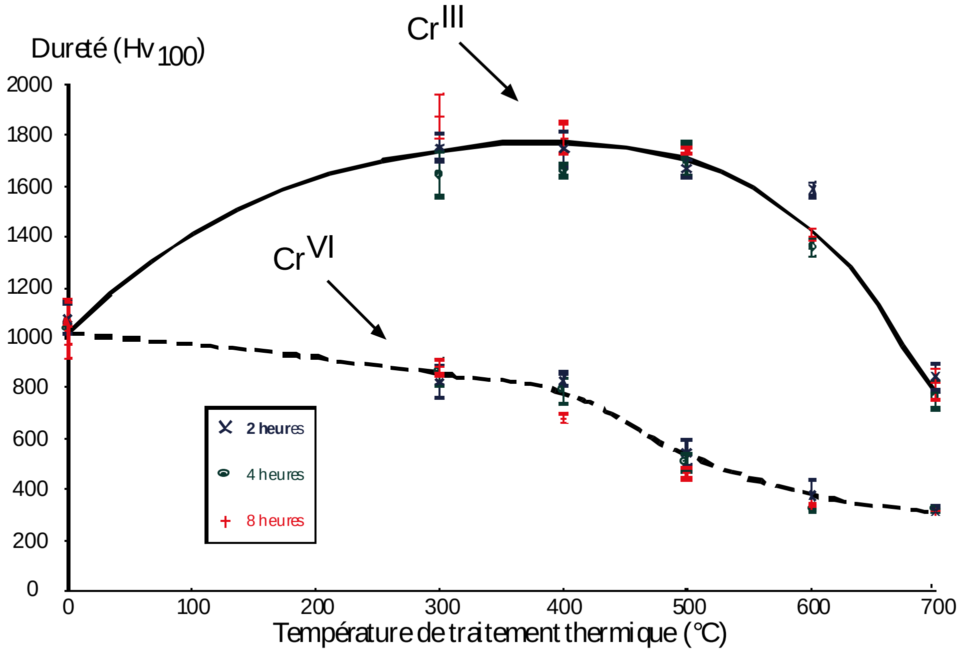

Fig. 10: Variation of Cr deposit (CrIII and CrVI) microhardness as a function of heat treatment temperature

V - Conclusions:

It is posible to obtain different type of deposits by electrodeposition from trivalent chromium bath. The composition of this bath is very simple the only difficulties (but important) is to use trivalent chromium ions obtained by reduction of hexavalent chromium : this reduction is very hazardous and must be done in a very safety manner.

However, results seems to be interesting. In particular, it appears that it is possible to obtain multilayers deposits: results we get with nickel-chromium compounds are for the moment not sufficient to use this type of materials as GMR materials but investigation are conducted now to decrease the size of the different layers, a thickness of about one nanometers would be certainly of a great interest in this field.

Also it is possible to obtain composite deposits with inclusion of particles as Al_2O_3 , SiC or PTFE with an homogeneous distribution : it seems that it is impossible to get this type of composite deposit by hexavalent chromium solutions, in this case, inclusions are in the microcracks of the hexavalent chromium deposit (increased cyclically by anodic etching).

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