Composite Nanomaterials : Contribution of Chromium Electrodeposition

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Abstract

Since 20 years, a great interest is focussed on nano-materials and application of electro-deposition to elaborate such materials for application in different fields of industry.

Since more than 15 years, we have developed a process to deposit hard thick chromium layers from trivalent chromium solution obtained by reduction of chromic acid.

We will present last results that we have obtained in the field of composite nano-materials obtained by co-deposition of chromium layers, using trivalent chromium solution, with sub-micronic hard and self-lubricating particles. Evolution of structure and transformation of crystal size will be shown when nano-particles are codeposited and we will shown also the nano-structure modification after heat treatment. Application of such materials will be described in particular in the field of mechanicals systems.

I – Introduction :

Many authors have described the electro co-deposition of particles of oxides, carbides, nitrides, metallic borides and organic compounds as PTFE. essentially in nickel and copper matrix. Particles, in general have a size varying from a few nanometers to a few tens of microns

For chromium plating, it exists some possibilities to make co-deposition of hard particles in chromium matrix : the major process, which is used at industrial scale, at our knowledge give very interesting results **(1-2).**

However, the process uses hexavalent chromium solutions and it is well known that chromium in hexavalent form is carcinogenic: new drastic regulations are or will be imposed in the near future.

It is well known also that due to electrochemical reasons, it is not a real co-deposition but a deposition inforced by using, in general, anodic phase during deposition processus.

This process uses also very high current density, addition cations and periodic and reversal current which allows to include hard particles in the microcracks of the deposit. So there is a non-homogeneous distribution of the particles. More, the concentration of included particles remains limited to a few percent.

However, despite all these imperfections in the deposits obtained, despite the fact that the hexavalent chromium solution is highly toxic and despite the fact that this co-deposition is difficult, the improvements in the physical properties of the chromium deposits with inclusions are so important that they justify the industrial use.

Some papers related to trivalent chromium deposition indicate that it is possible to obtain composite deposit but cross-sections of the resulting deposits show very brittle deposit and in major cases non-adherent deposit.

Following our research works on hard trivalent chromium deposit through trivalent chromium ions obtained by reduction of chromic acid by an alcohol such as methanol **(3)**, we have investigated the possibility of preparing composite chromium deposits with inclusions of hard particles such as alumina (Al_2O_3) particles and we are testing co-deposition of self-lubricating particles such as PTFE..

II – Hard thick trivalent chromium :

We have described in earlier publications that it is possible to obtain thick hard chromium deposit by using an aqueous trivalent chromium solution obtained by reduction of CrO_3 by methanol in chloride medium. This reaction is very hazardous and it is strongly recommanded to take the maximum of care during the completion of the oxido-reduction reaction which is highly exothermic.

Through the trivalent chromium solution it is possible to obtain hard thick deposits with large thickness (more than 100µm) with a microhardness of about 1000HV/100g load.

The concentration of chromium in the solution is about 60 g/L and we use boric acid as buffer, chloride or sulfate alkaline salts as conductive salts and some wetting agent as Fumetrol®.

The rate of deposition is about 3µm/mn at a current cathodic density of 80 A/dm² and temperature of the bath 50°C.

We show in the figure 1 some aspects of deposits obtained: pictures are from optical microscopy (O.M.) on cross-sections . Thicknesses in the present case are varying from 25 to 50 µm and there are cracks through the deposit, the microhardness has been measured to be between 900 and 1000 HV/100g load

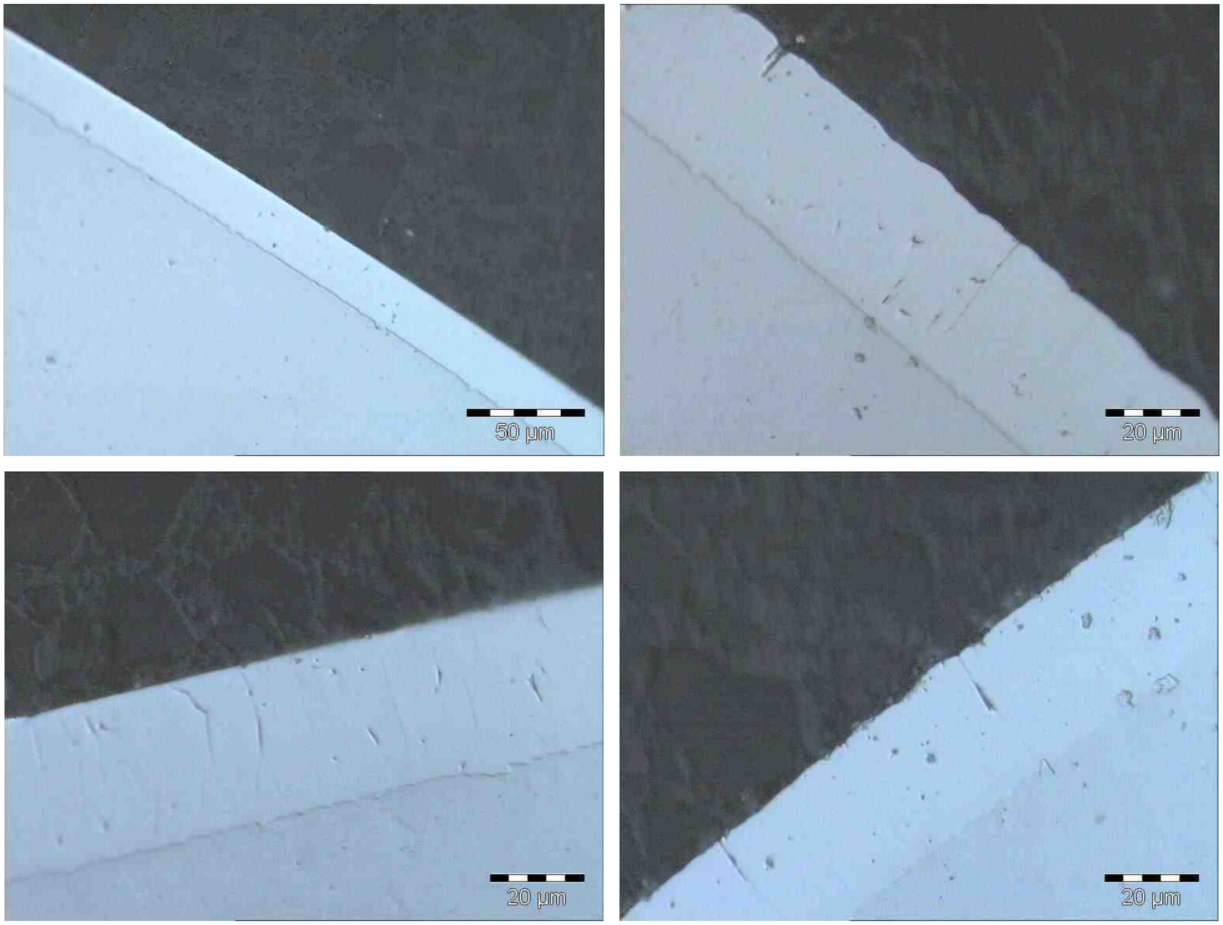

Figure 1 : Cross-sections of hard thick trivalent chromium on steel substrate

II – Codeposition of Al_2O_3 particles in chromium layers

To investigate the feasibility to obtain composite deposits with chromium matrix, we have used the same trivalent chromium solution as for hard thick chromium deposition and we have included in the solution hard particles as Al_2O_3.

For hard particles we used Al_2O_3 with size between 0.1 and 3 µm. The preparation of the solution was done by only rinsing the particles in HCl 1 N medium and then introducing the particles in the trivalent chromium solution under constant agitation..

We have also tried co-deposition of PTFE particles : we used as agent for particles, a solution used in PTFE electroless Nickel deposition. Due to wetting agent(s) include to allow PTFE particles emulsion, it is necessary to acidify the solution to avoid increasing pH value. We present in the following pictures (figure 2) different results that we obtained on cross section by optical microscopy.

Using the same conditions as for pure chromium deposition (80 A/dm², temp. 50°C, pH about 0), it is possible to obtain composite deposit without difficulties **(4).**

It is interesting to note :

- first the presence of particles in the deposit with an homogeneous repartition
- also the thickness of the deposit : about 100 µm.

We have measured the microhardness of the deposit and the result is about the same as without particles : 900 to 1000 HV/100g even in the case of hard particles.

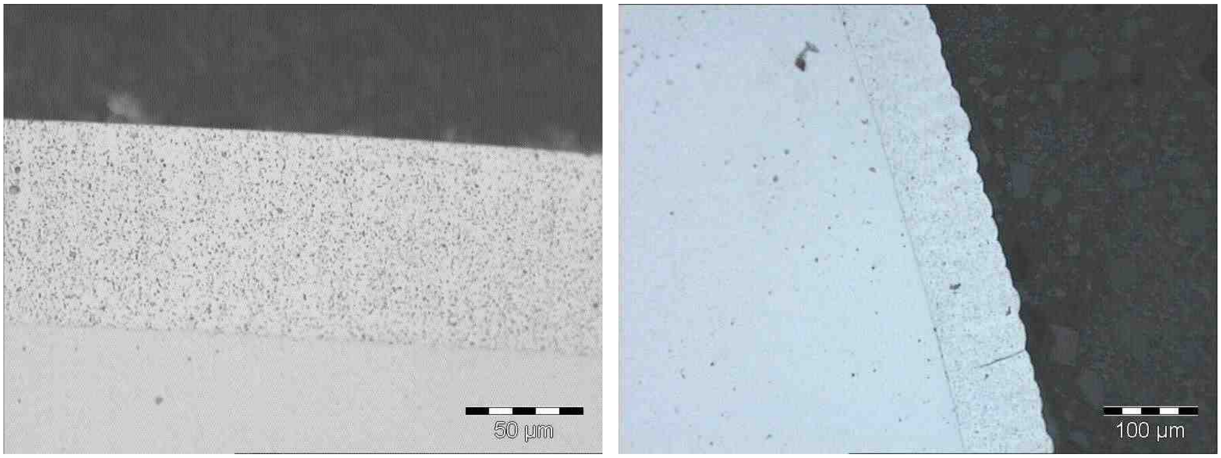

Figure 2 : Cross-section of Chromium+particles of Al_2O_3 on steel substrate (M.O.)

***Influence of particle concentration* :**

We have made a study of the influence of the concentration of Al_2O_3 particles in the solution on the particles concentration in the deposit by increasing the concentration of the solution in Al_2O_3 (in mass) from 2 g/l to 20 g/l . The value of the concentration in the deposit has been measured by the ratio on a cross section of the two surface : total particles and deposit.

In the following (figures 3-6) obtained by SEM examination, are shown the different cross section of chromium composite deposits obtained with different composition of the solution.

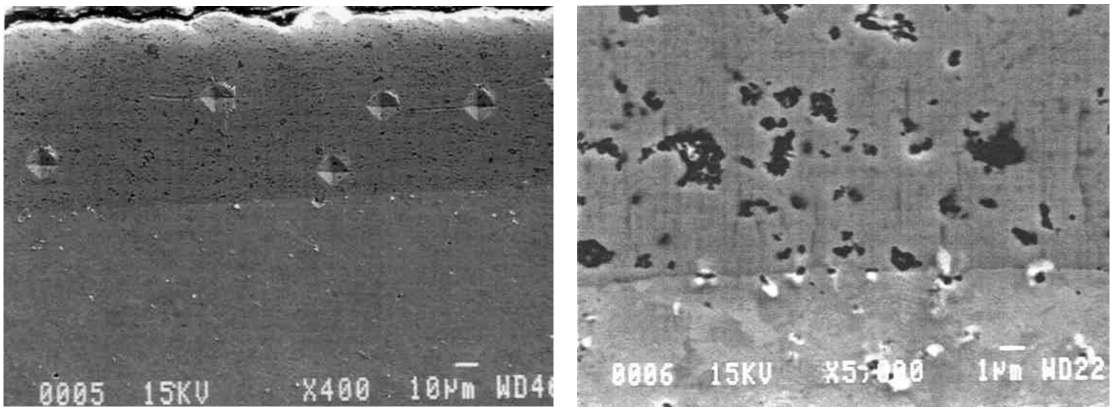

Figure 3 : Trivalent chromium deposit with Al_2O_3 particles
(Bath concentration in particles : 2 g/l)

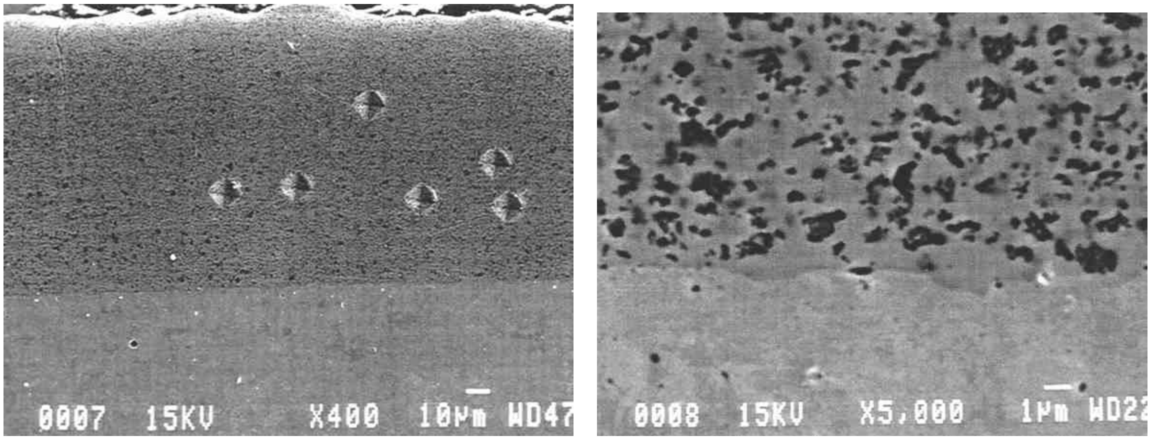

Figure 4 : Trivalent chromium deposit with Al_2O_3 particles
(Bath concentration in particles : 4 g/l)

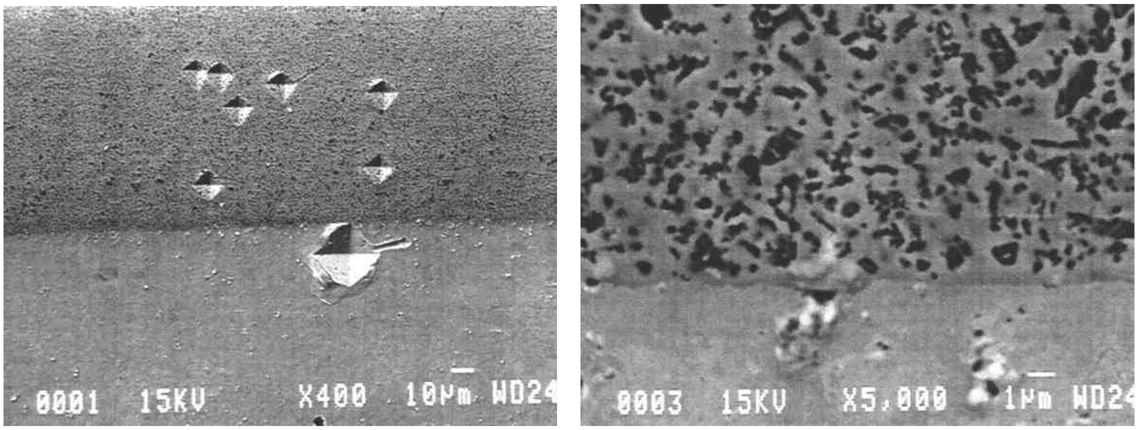

Figure 5 : Trivalent chromium deposit with Al_2O_3 particles
(Bath concentration in particles : 10 g/l)

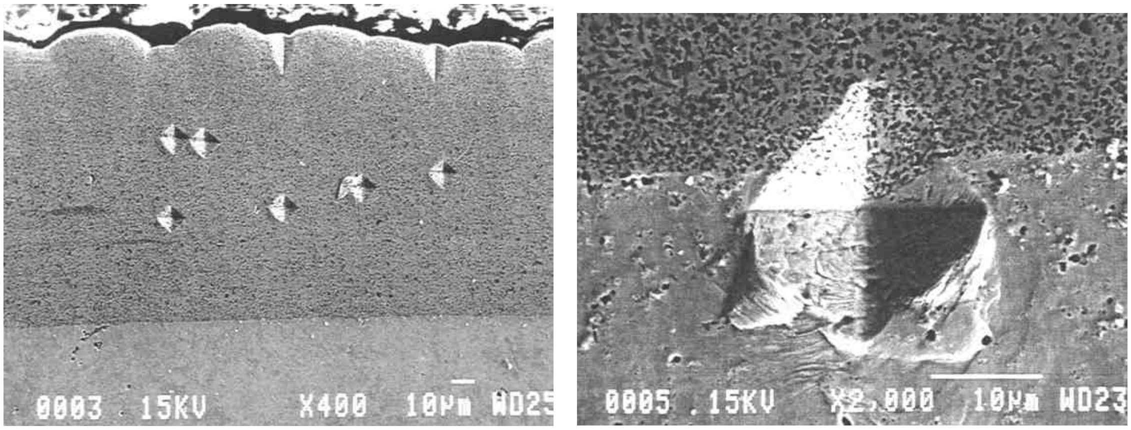

Figure 6 : Trivalent chromium deposit with Al_2O_3 particles
(Bath concentration in particles : 20 g/l)

N.B. : There is no cracks between the deposit and the substrate
in the microhardness indentation in figure 6

For each concentration it is possible to see the Vickers indentations. In the figure 5 (Al_2O_3 concentration 10 g/L), it is possible to compare the indentation in chromium deposit and in the substrate .
In the picture 6 (Al_2O_3 concentration 20 g/l), it is possible to see the interface between Cr + Al_2O_3 and the substrate which appears without de-cohesion of the layer after indentation which is the indication of an excellent adhesion.

In the following two spectra (figure 7-8) obtained by X-ray fluorescence microanalysis, comparison of the two spectra evidency the presence of aluminium: it is possible to see presence of aluminium in the deposit due to Al_2O_3 particles (figure 8) and sure also chromium in one of deposit

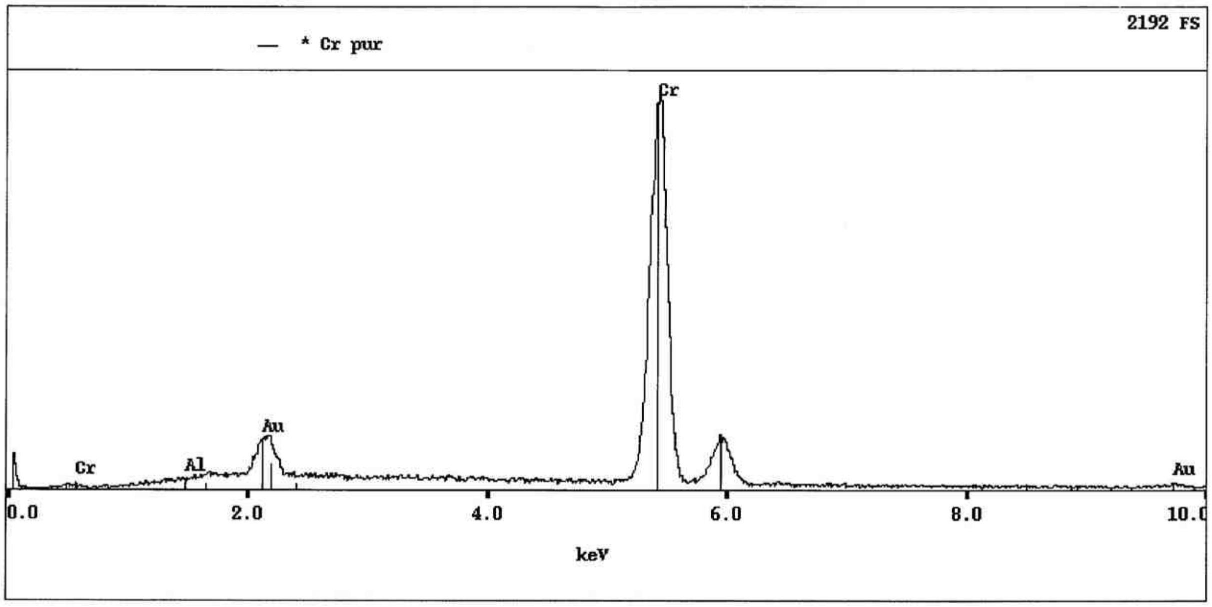

Figure 7 : Fluo X-ray spectrum of deposit zone without Al_2O_3 particles (Au is due to metallisation before examination)

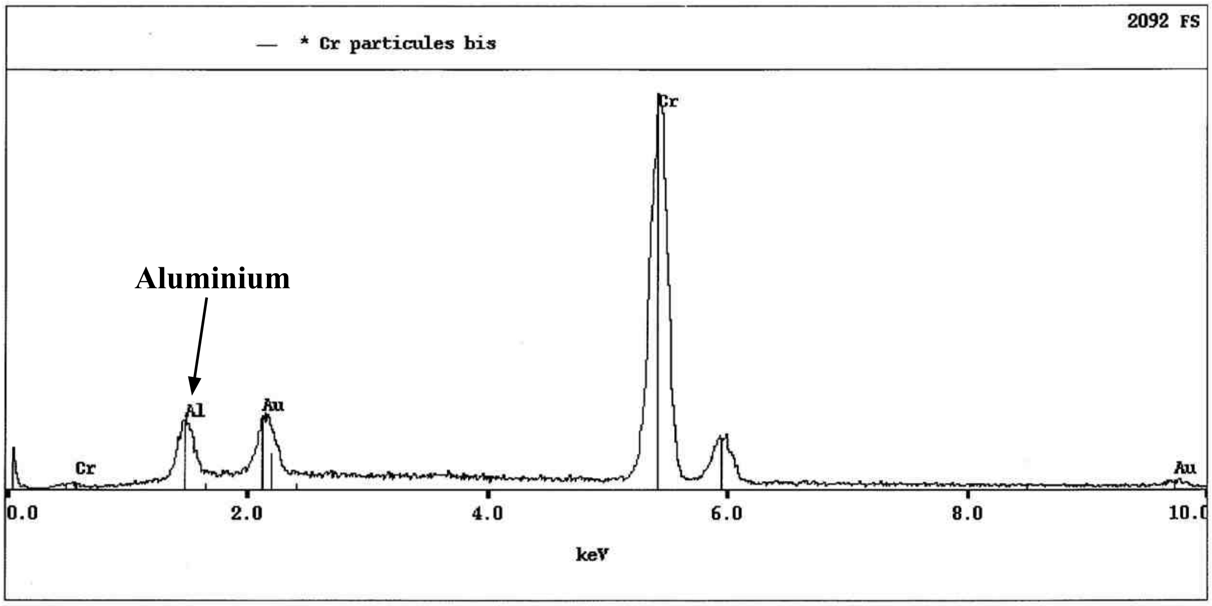

Figure 8 : Fluo X-ray spectrum of deposit zone with Al_2O_3particles

In the following figure 9, the curve gives the variation of the particles concentration in the deposit (measured by the relation between total surface of the particles to total surface of the cross section of the deposit) versus bath particles concentration.

It is interesting to note that there is a flat part in the curve when the Al_2O_3 concentration in the bath is more than 10 g/l which correspond to a concentration of about 20-22 % in the deposit.
This phenomena is very interesting because concentration in the deposit will remain about the same even the concentration in the solution varies from 10 to 20 g/l (in case of heterogeneous solution due to a lack of agitation during application).

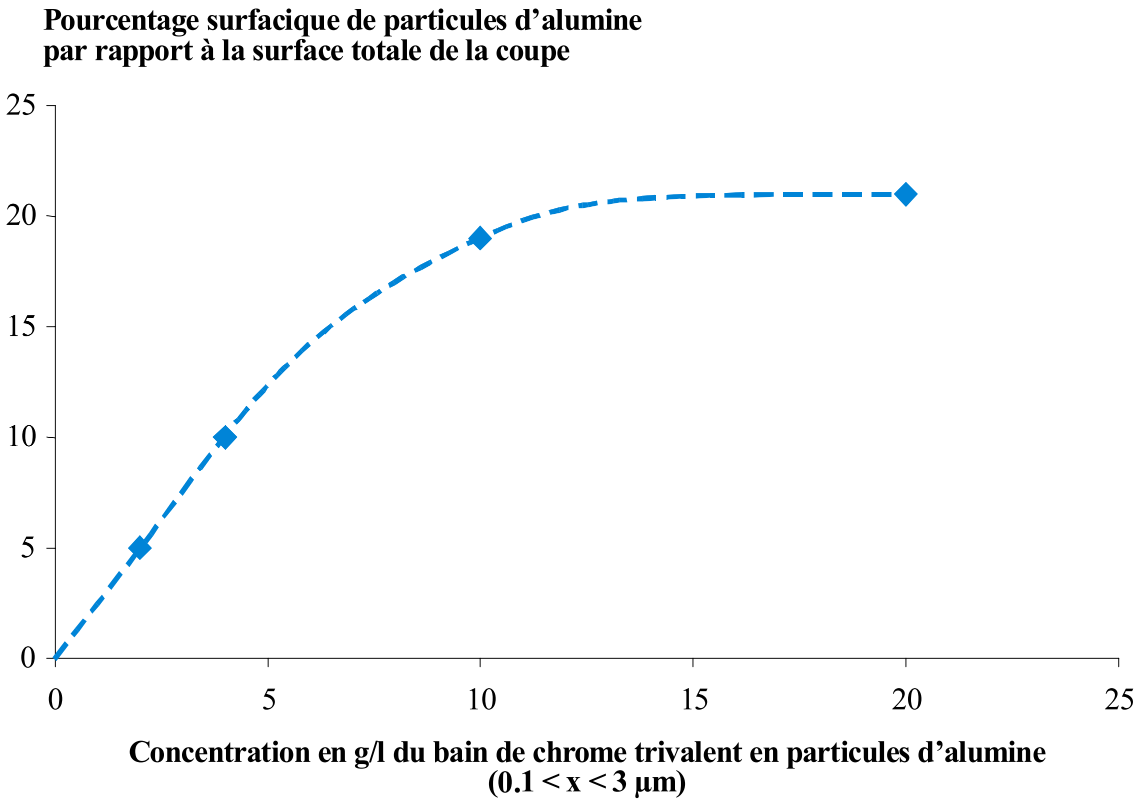

Figure 9 : Variation of the particles concentration in the deposit vs bath particles concentration.

III – Evolution of structure after heat treatment

It is also well known **(5, 6, 7)** that deposits obtained by trivalent chromium solution present an evolution of the microstructure when they are heat treated. To have a better understanding of the different phenomena, X-ray diffraction has been used to know the structure evolution after heat treatment. For the moment we have studied this influence only on "pure" chromium deposit.
In the following spectra (figure 10-11) we show the variation of the structure after a heat treatment of 350°C during 1 hour in an inert atmosphere (Argon gas).
The different spectra (figure 10 – 11) show interesting results :

- as deposit (figure 10), the size of the crystal is very small (Cr peak FWHM very large), it appears as "amorphous-like" structure. As comparison, Cr(VI) deposits have a well-ordered structure **(8)**,

- a slight shift in the Cr peak position indicates some residual strength in the deposit,
- after heat treatment (figure 11), the micro-structure of the deposit changes radically with Cr crystal formation (sharp Cr peak) and a real microstructure of chromium deposit.

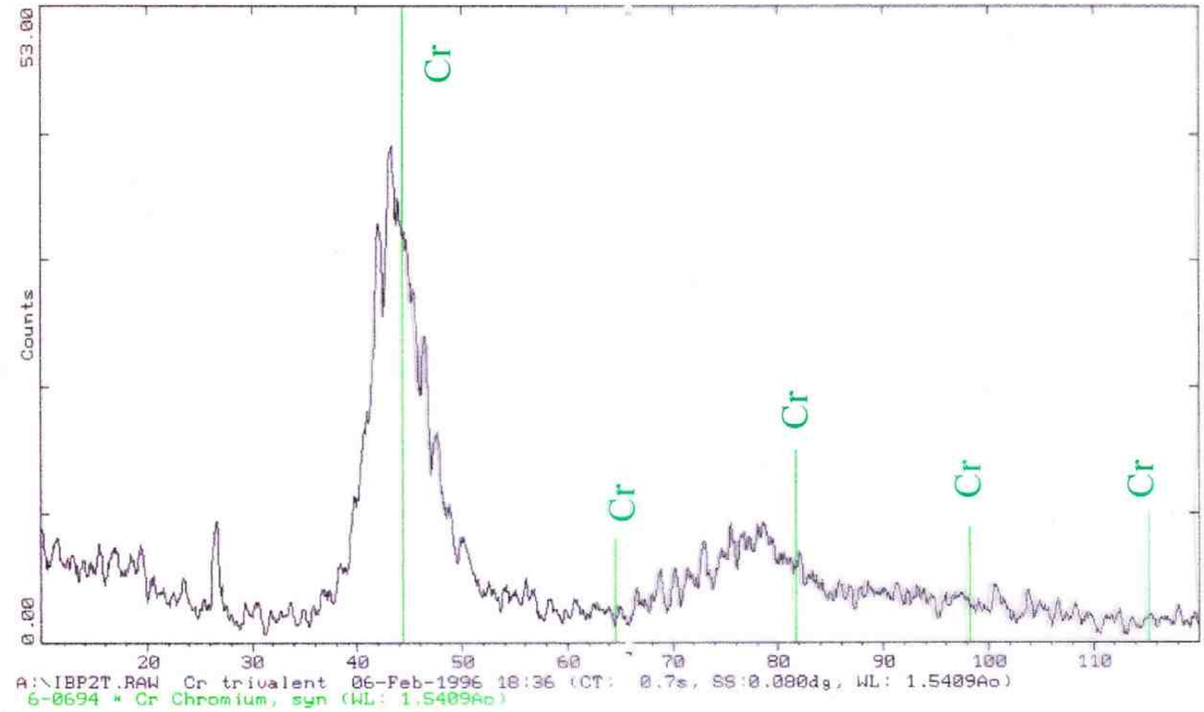

Figure 10 : X-ray spectrum on as deposit chromium (without particles) from Cr(III) solution.

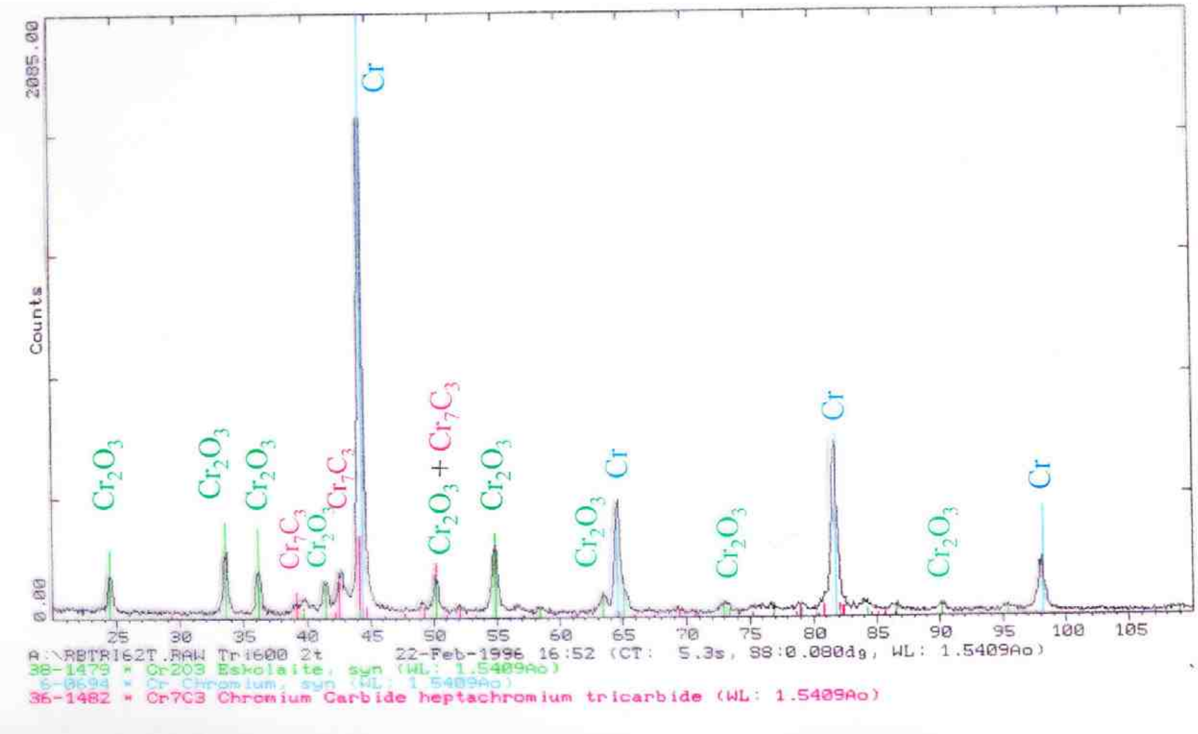

Figure 11 : X-ray spectrum on heat treated (1h-350°C) (without particles) chromium from Cr(III) solution

Evidently, it appears in the spectrum of chromium deposit, after heat treatment, the presence of Cr_7C_3 and also Cr_2O_3. To our knowledge, Cr_2O_3 is due to oxidation after heat treatment and Cr_7C_3 is due to formation of chromium carbide during heat treatment. The formation of Cr_7C_3 due to presence of Carbon in the deposit which is a characteristic of Cr(III) deposition, explain also the increasing value of the micro-hardness.
In the X-ray spectrum there is no presence of $Cr_{23}C_6$.

To evidency more strictly presence of Cr_7C_3, we have dissolved the chromium deposit after heat treatment in HCl medium. A black powder, resulting from chromium deposit dissolution has been isolated and tested by X-ray diffraction.
The spectrum is shown in the following figure : Cr_7C_3 appears as Cr_2O_3 and also Iron oxides due certainly to slight dissolution of the substrate.

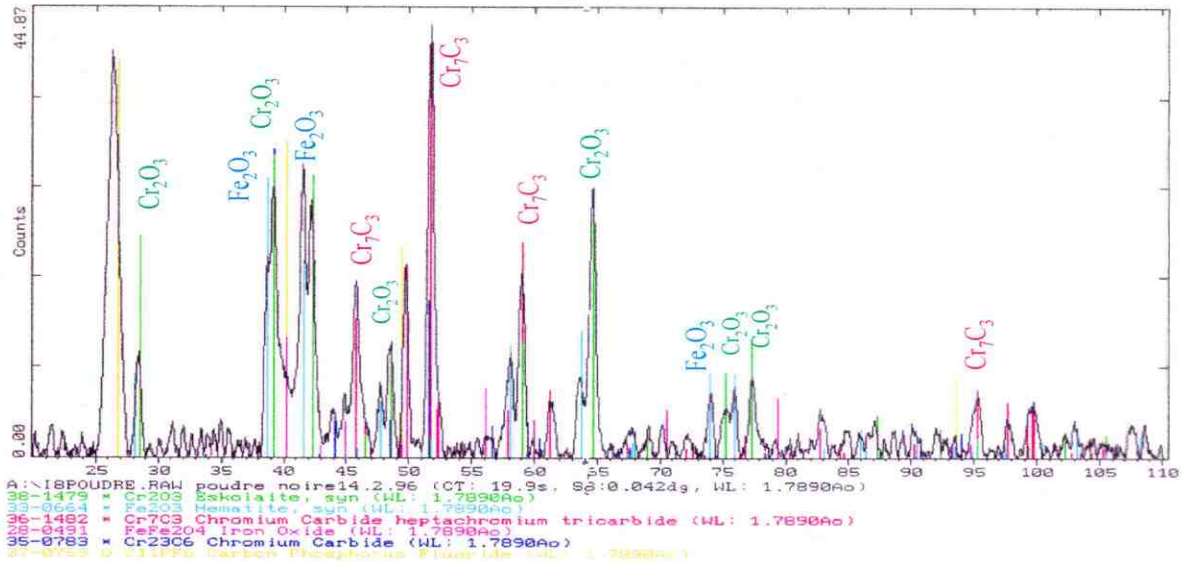

Figure 12 : X-ray spectrum on heat treated (1h-350°C) chromium after dissolution in HCl medium - Compounds present : Cr_7C_3, Cr_2O_3, Fe_2O_3

To follow the variation of the structure during heat treatment, chromium deposit sample has been heated in an oven, with controlled athmosphere, X-Ray diffraction spectra have been registered during the heat treatment and associated temperature has been registered by an IR video camera. By this method it has been possible to evidency the evolution of chromium layer structure during heat treatment **(9).** The principle of the apparatus is shown in the figure 13 and the result obtained on chromium layer is given in figure 14.

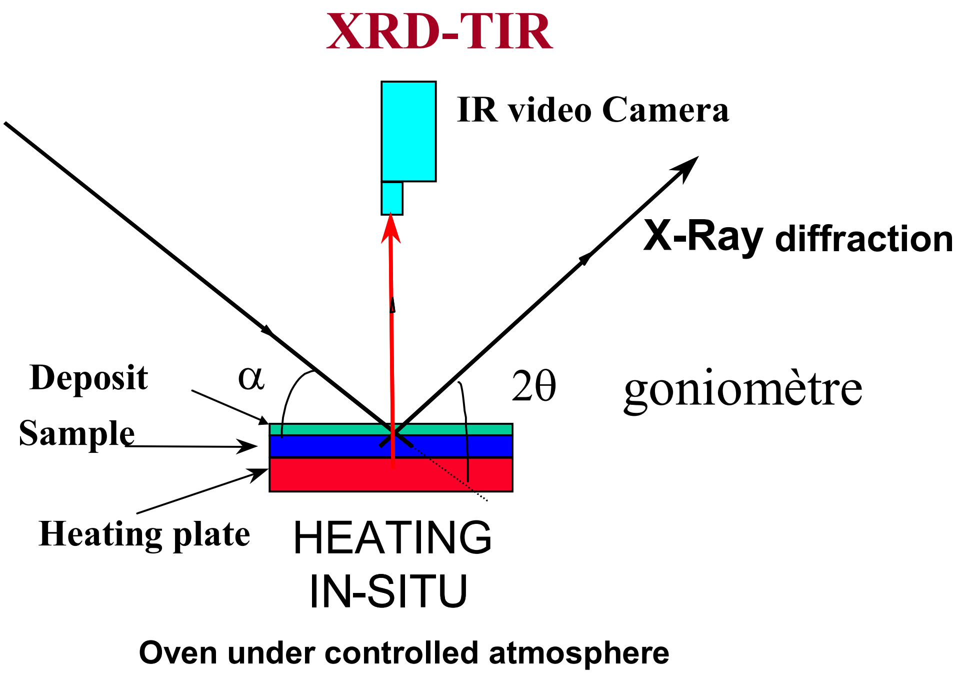

Figure 13 : Schema of the X-Ray diffraction system "In-situ"

Results obtained during heating of a chromium (CrIII) deposit are shown in the following figure 14. The evolution of the structure appears clearly:

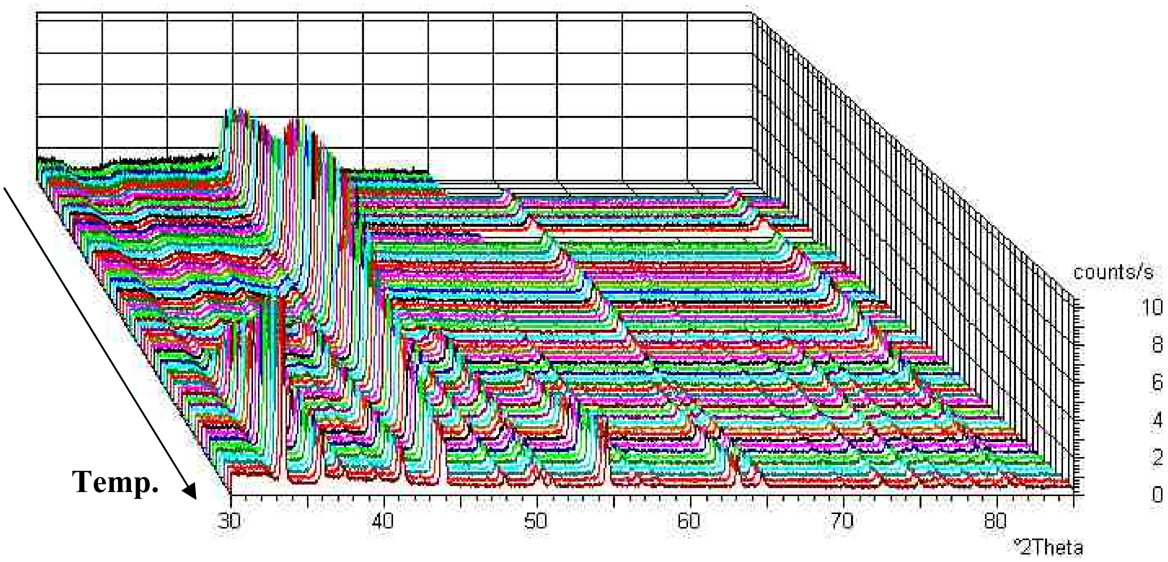

Figure 14 : evolution of the microstructure as a function of temperature

IV - Variation of the microhardness after heat-treatment :

As a consequence of micro-structure evolution of chromium deposit from a trivalent solution, it is also well-known that there is an important increase in the micro-hardness of the deposit.

The variation of micro-hardness of trivalent chromium deposit is shown in the following figure 15 as a function of temperature of heat treatment and duration of the treatment **(10).** The curves indicate the comparison between variation of micro-hardness deposits obtained from trivalent and hexavalent solution : results show that deposits obtained from trivalent chromium present a high value of micro-hardness (1700 – 1800 HV/100g) although in the same time deposits from hexavalent chromium solutions present an important decreasing value.

The variation of the micro-hardness is due to different phenomena or effect and follow different laws:

- the Hall – Petch law which indicates that the micro-hardness is an inverse function of the crystal size (until crystal size reach value of about 8 – 10 nm): in the case of chromium it has been demonstrated that the function is an inverse of the square root of crystal size **(11)**,
- the pin effect which is the result induced by insoluble compounds in chromium structure (in our case essentially Cr_7C_3) which migrate at the grain boundaries impeding the migration of lacunes (blocking effect) and so increase the hardness.

It is interesting to note, following the results, that the micro-hardness of the Cr deposit is about in the same range as some physical deposits.

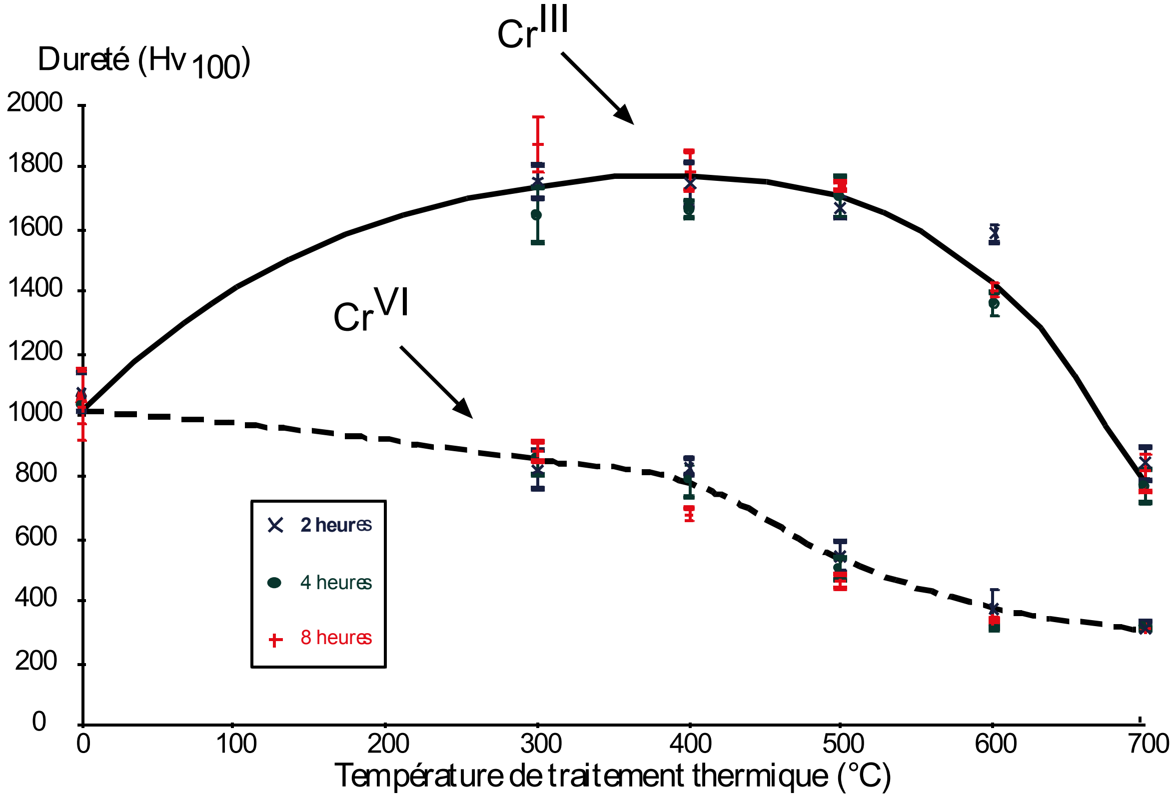

Figure 15 : Variation of the Vickers microhardness of Cr deposit (Cr(III)) (without particles) as a function of heat treatment temperature and duration time (2, 4 , 8 hours)

Following are SEM figure of Cr deposit from a trivalent chromium aqueous solution after heat treatment.

In the figure 16 we present SEM pictures of Cr (without particles) cross-section, after heat treatment (300°C, 1h) : it is possible to see Vickers indentation (100 g load) on the cross-section.

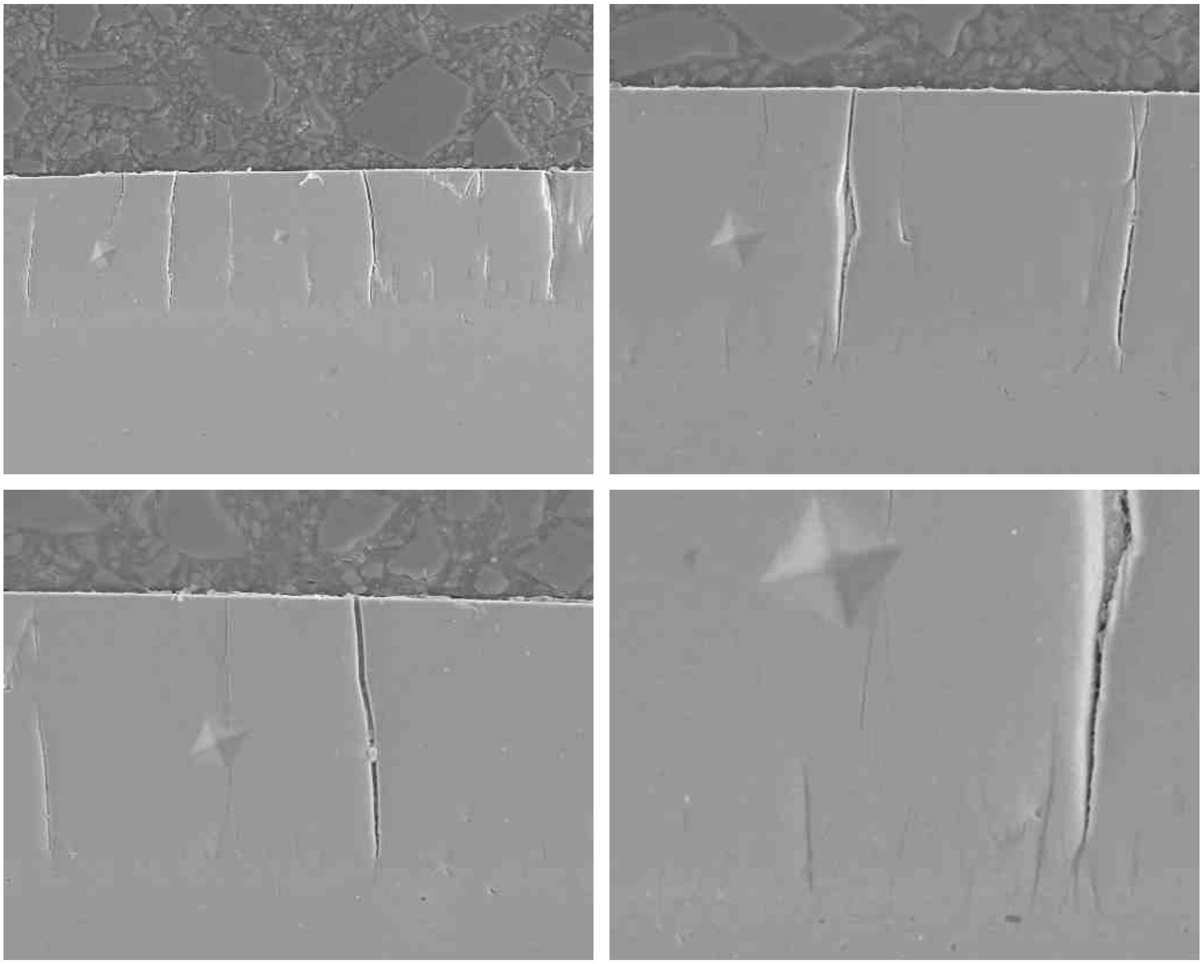

Figure 16 : SEM pictures of "pure" chromium : note micro-cracks through the deposit and the size of the Vickers indentation (100 g load)

In the same way, in the following figure 17 are presented SEM picture of Cr + Al_2O_3 particles deposits after heat treatment :

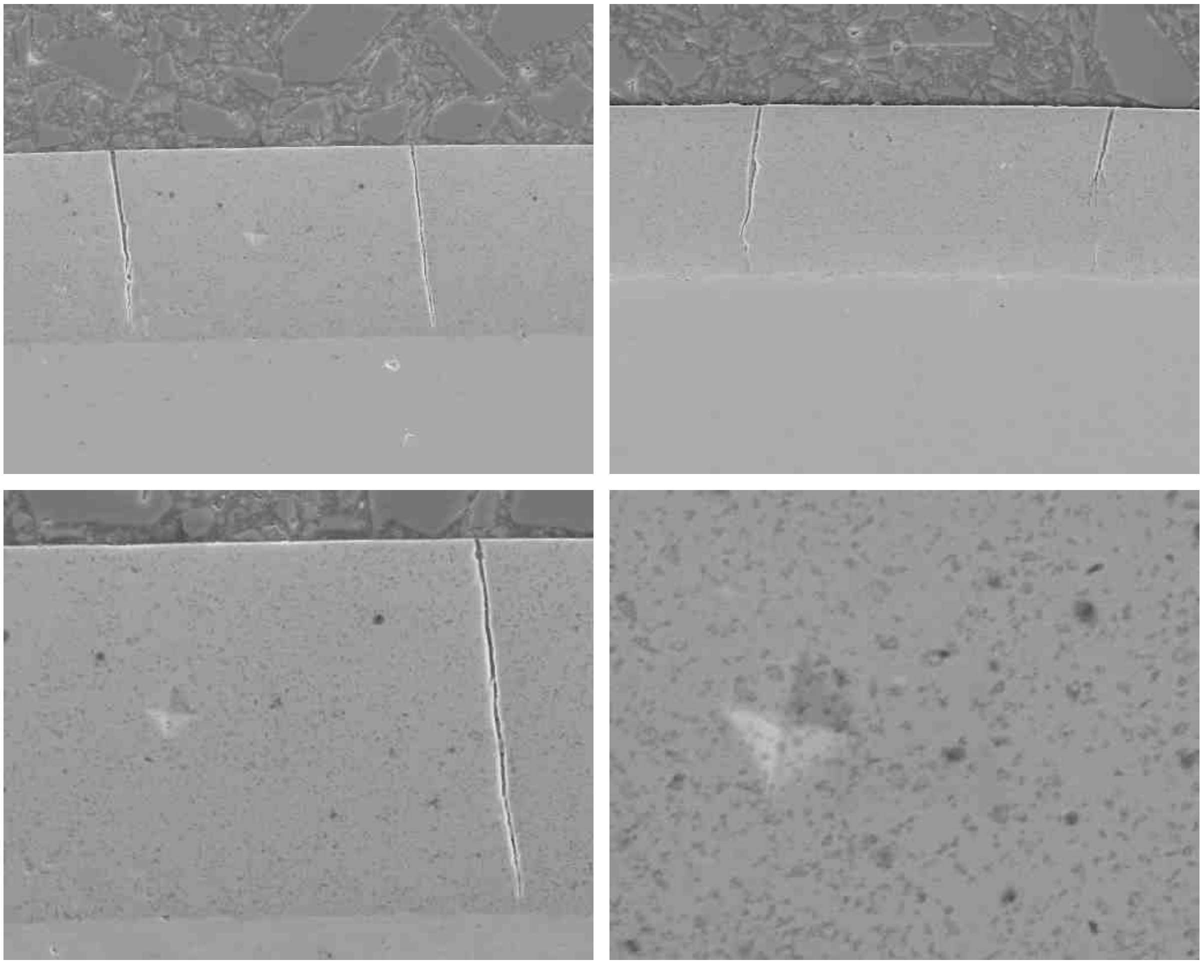

Figure 17 : SEM pictures of composite chromium (Al_2O_3particles) :
note the small size of the Vickers indentation (100 g load).

V - Conclusions :

Chromium deposit from a trivalent chromium solution obtained by reduction of CrO_3 present some interesting particularity from deposit obtained from hexavalent chromium solution :

- microstructure "as deposit" are different : amorphous like structure for Cr(III) instead of structured deposits from Cr(VI) bath where crystal orientation is a function of the different parameters : bath temperature, cathodic current density…
- possibility of homogeneous composite deposits (inclusions of particles) which allow to have special comportment and tribological characteristics,
- structural modification by heat treatment increasing the micro-hardness until values in the range of PVD deposits but with a well known excellent adhesion, characteristic of electrodeposition due to crystal growth phenomena.

In spite the fact that until now, hard thick trivalent chromium processes are not so easy to be industrially applied compare to hexavalent chromium processes and present some restrictions in the application (due to complexity of trivalent chromium chemistry) in particular the throwing and covering power, it appears that the characteristics of the Cr(III) deposits seems to be attractive in a near future.

Some recent programme on trivalent chromium deposition are on the way and could bring to surface finishing industry a response to a scoured question : are trivalent chromium processes industrially viable ? …

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