Hard Chromium Films Produced by Electrolytic Process on Low Steel Substrates

Younès Benarioua[1,2](✉), Younès Kermiche[1], and Selma Baali[1]

[1] Department of Mechanical Engineering, Faculty of Technology, University of M'sila,
Bordj Bou Arréridj Road, 28000 M'sila, Algeria
`benariouayounes@yahoo.fr, younes.benarioua@univ-msila.dz`
[2] Unité de Recherche Matériaux Emergents, Compus El Maabouda Université de Sétif 1,
Sétif 19000, Algérie

Abstract. Generally, wear and corrosion problems that appear on the surface of metallic materials can degrade them and reduce their lifetimes. Therefore, a surface treatment that corrects these objects without affecting their characteristics is more effective than replacing the entire material. Hard chrome is considered one of the most interesting coating materials for increasing wear and corrosion resistance, as well as extending the service life of mechanical parts used in many industrial applications, such as petrochemical, oil and gas. In this work, a growth kinetic study of a hard chromium coating obtained on low-carbon steel substrates by an electrolytic process in a trivalent chromium bath heated to a temperature of 50 °C for an immersion time ranging from 10 to 50 min with a 10 min step was conducted. The structure, morphology, thickness and hardness of the coating obtained by various immersion times have been analyzed respectively by X-Ray diffraction, micrographic observation, and micro-hardness test.

Keywords: Chromium · steel · electrolytic · immersion time · coating

1 Introduction

During the last few years, the use of hard metallic coatings as chrome plating treatment to improve the chemical and mechanical behaviors of work parts has shown an extensive development [1–4]. Soft and hard chromium are two types of chrome plat-ing that have been commonly applied to the industry. Soft chromium (decorative) has been employed to malleable steel components in providing a chromium layer against corrosion [5, 6]. Contrary to the first one, hard chromium applied to hard steel parts, providing good aesthetics, brightness, and resistance against wear and corrosion. Hard chromium plating is a widely used technique to improve the wear and corrosion resistance of tools and mechanical parts [1–6]. It is applied widely in several industry fields as automotive, hydraulic cylinders, machine tools and aerospace [7].

Hexavalent hard chromium has been widely used as functional electroplating materials in several industrial fields [1, 2]. Despite the stability and reliable quality it presents, hexavalent chromium is toxic and hazardous to the environment. However, this type of

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coating has very restricted use due to environmental laws in some countries. In order to avoid the problem, it is necessary to replace hexavalent chromium plating with trivalent chromium plating [5, 6]. In this study, the hard chromium coatings produced from an electrolytic bath of trivalent chromium exhibit a particular electrochemical behavior whose active dissolution domain is absent in acid solution.

Reaction-diffusion laws govern the formation and growth of metallic coatings deposited chemically on metallic materials [8]. Several authors have studied the formation and growth of metallic or intermetallic layers deposited on metallic supports during heat treatment or thermochemical treatment [9–11]. The objective of this work is to study the formation and growth of the hard chromium coating deposited on low-alloy steel 20CN6 using the electrolytic technique. Based on the immersion time which is considered as the technological parameter and the corresponding thickness, the determination of chromium layer formation can be controlled either by diffusion or by arrangement. The structure, the morphology and the hardness of hard chromium coating were investigated by different means and methods of analysis.

2 Experimental Details

The steel substrates take cylindrical shape of 20 mm in diameter and 10 mm in height. The chemical composition of used steel in weight % is: 0.19% C, 1.12% Cr, 0.38% Ni, 0.20% Cu, 0.14% Mn, 0.12% Si, 0.07% Mo. To obtain chromium deposits with better adhesion and thickness homogeneity, it will be useful to prepare mechanically and chemically the surface of the substrates. The samples were polished using abrasive paper and diamond pastes. To remove oxide layers adhering to their surfaces, the steel samples were decreased during 10 min in a solution of sulfuric acid heated at 50 °C. The hard chromium coating was then performed using a standard electrolytic procedure in an industrial bath, constituting the anode in alloyed lead (Pb-7%Sb) connected to the positive pole and the cathode, which is the steel sample, connected to the negative pole. The deposition parameters used for the various operations are as follows: Current density of 10 A/dm^2 applied to the electrolytic solution heated at 40 °C and composed of chromic oxide (250 g/l) and sulfuric acid (2.5 g/l) as catalyst in 100/1 ratio. The immersion time of the treatment chosen as the only technological parameter in this study varied from 20 to 50 min with a step of 10 min. In these conditions and according to the treatment durations, the produced coatings are composed of pure chromium and have various thicknesses. The samples (chromium/steel) were sectioned, polished, and etched with a chemical reagent composed of 100 ml of water, 2 ml of 40% HF (hydrofluoric acid), and 5 ml of 30% H_2O_2 (hydrogen peroxide). The thickness and morphology of the chromium layers were observed using an Olympus B O71 optical microscopy. The structure of the samples was revealed by the use of a Phillips diffractometer. The characteristic radiation is Cu Kα with a wavelength of 0.15418 nm and the diffraction angle 2θ varies from 40 to 120°. The cross-sectional hardness profile of the samples was obtained using a Leco micro-indenter.

3 Results and Discussions

3.1 Structure

Figure 1 shows the X-ray diffraction pattern revealing the chromium phase formed on the surface of two substrates coated for immersion time of 20 and 50 min. For a sample treated at high immersion time, the peaks of chromium phase present exalted peaks (110), (211) and (310) relative to those of chromium of sample treated for holding time of 20 min which present lower diffraction intensity. The gradual thickness of chromium layers increases with the increasing immersion time which is from 10 to 50 min. The variation in the intensity of the diffraction peaks corresponding to the chromium coating shown in the figure below may reflect this type of graduation.

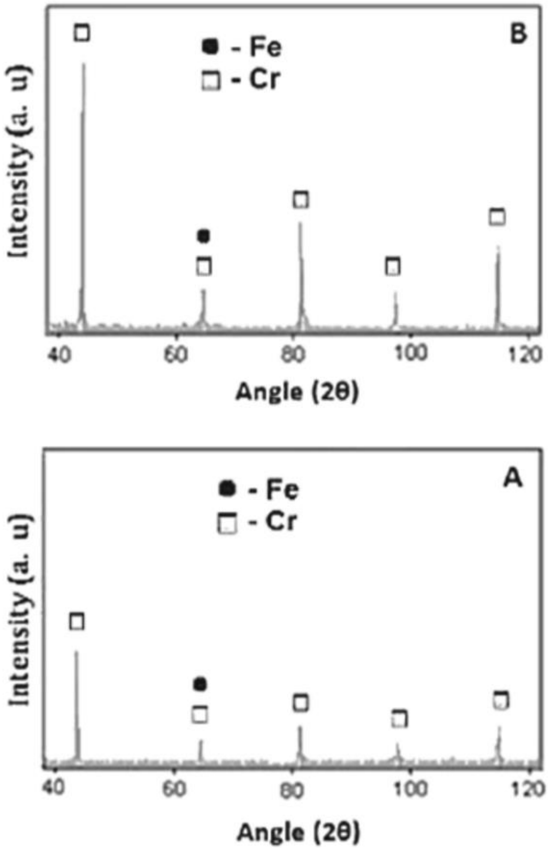

Fig. 1. Diffractograms of chromium coating on steel for immersion time of 20 min (A) and 50 min (B).

3.2 Morphology and Thickness

The cross-sections of optical micrograph coated samples at bath temperature of 50 °C for the immersion time of 20, 30, 40 and 50 min are shown in Fig. 2, where the white chromium film is clearly visible. The microstructure of the chromium layers corresponding to all samples presents an almost uniform state and shows a nearly dense coating. The chromium coating seems to be adhesive to steel substrate, in fact the coating follows perfect profiles to substrates and there are no defect and voids between the substrate and the deposit.

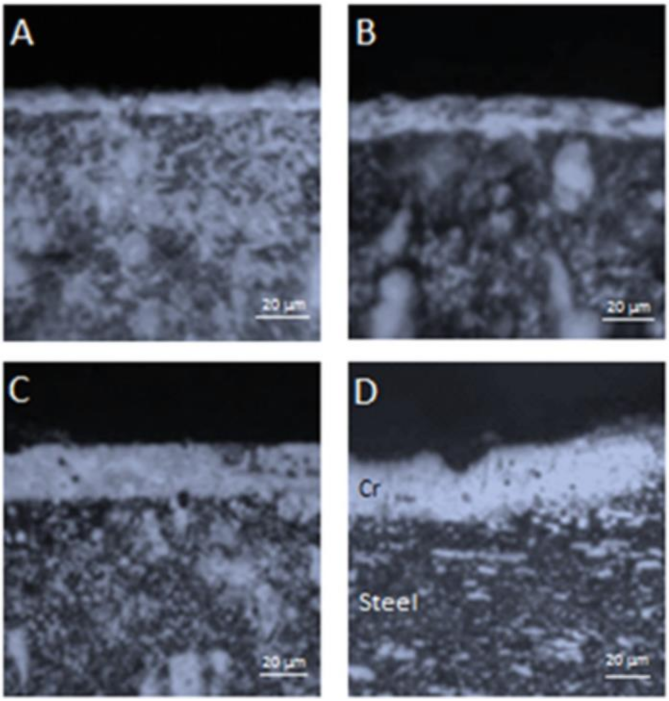

Fig. 2. Optical photographs of chromium coatings on steel substrates obtained in bath immersion time of (A) 10 min, (B) 20 min, (C) 40 min and (D) 50 min.

Figure 3 presents the increase of thickness chromium layer with the increasing of the time of treatment and the curve corresponding to this variation takes the parabolic form.

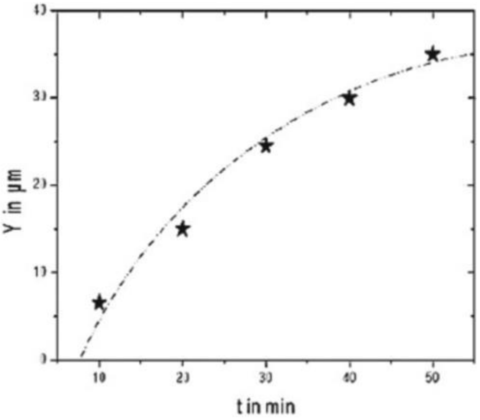

Fig. 3. Variation of chromium coating thickness with immersion time treatment

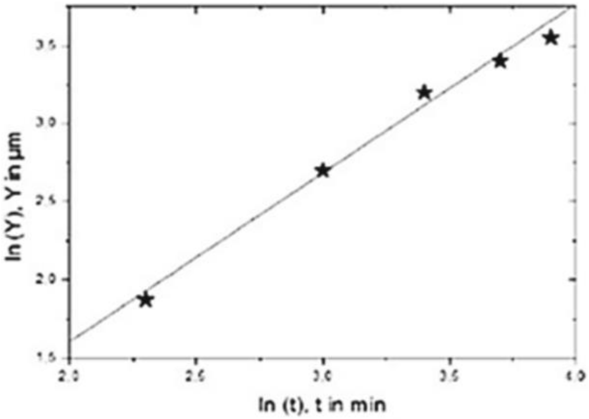

Fig. 4. Variation of chromium coating thickness in function of bath Immersion time in bi-logarithmic scale.

3.3 Growth Kinetic

To determine the growth kinetic of chromium coatings, a sample power low expressing the growth equation used to clarify the growth rate data as follow

$$Y = K.t^n \tag{1}$$

where Y represents the coating thickness (µm) and t is the time of immersion (min), K is the growth rate constant and n represents the growth rate time exponent.

$$Ln Y = Ln K + n Ln t \tag{2}$$

The representation of Eq. (2) on logarithmic scales of the thickness of layer Y as a function of immersion time t, representing experimental data, exhibits a linear pattern as shown in Fig. 4. We can conclude that Eq. (1) satisfactorily represents the experimental data.

The growth time constant n indicates the kind of kinetic relating to the growth of the coating. When n takes values close to 0.5, the kinetics representation is parabolic; the layer growth is controlled by diffusion. When n takes values close to or equal to 1.0, the progression kinetic of the coating has a linear representation; the growth in this case is controlled at the interface.

In our case, the value of the constant n related to chromium coating is equal to 0.5 thus confirming that parabolic diffusion is the process which governs the growth kinetics of the chromium coating. This is in line with Faraday's first law of electrolysis.

This last describes that the mass or amount of substance (chromium) to be deposited on the electrode as steel substrate is directly proportional to the amount of electricity passing through electrolytic solution. The amount of electricity is characterized by the electric current and the time of treatment. In this case, the time of immersion has an effect on the growth kinetic of chromium coating in the presence of the current which considered as constant parameter.

3.4 Hardness

Figure 5 presents the histogram of chromium coating hardness in function of immersion time. The hardness measured perpendicularly is performed on the surface of the coatings under an indentation load of 100 g.

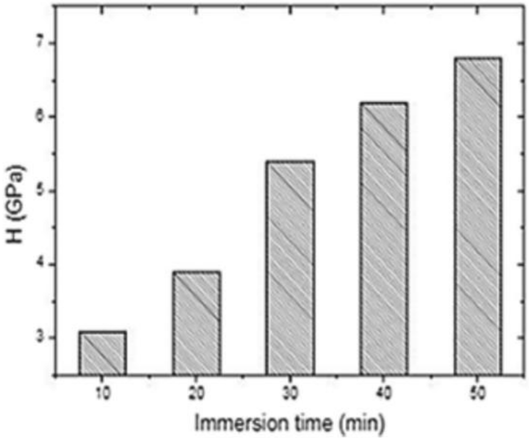

Fig. 5. Hardness variation of chromium coating as a function of immersion time

The histogram in Fig. 5 increases with the increasing time of treatment. This indicates that the hardness of coatings treated at high immersion time is preponderant relative to that obtained at low time of treatment. The high thickness produced at elevated immersion time was responsible for high hardening comparative to that obtained at the sample treated for low treatment time, this last result hardness corresponding to the composite (coating/substrate) but not to the only chromium coating.

The hardness of the plated chromium increased from 3.10 to 6.80 GPa as the holding time from 10 to 50 min. For a low immersion time where the thickness of chromium coating is small, the steel substrate has a strong contribution to the hardness measured. The effect of substrate on the hardness obtained undergoes a decrease when the time of immersion is high. However, the thickness of the chromium layer becomes important and would be responsible for the hardening observed. Figure 6 shows the results of the hardness profile of the chromium layers obtained in an electrolytic bath for different immersion times by using an indentation load of 1N.

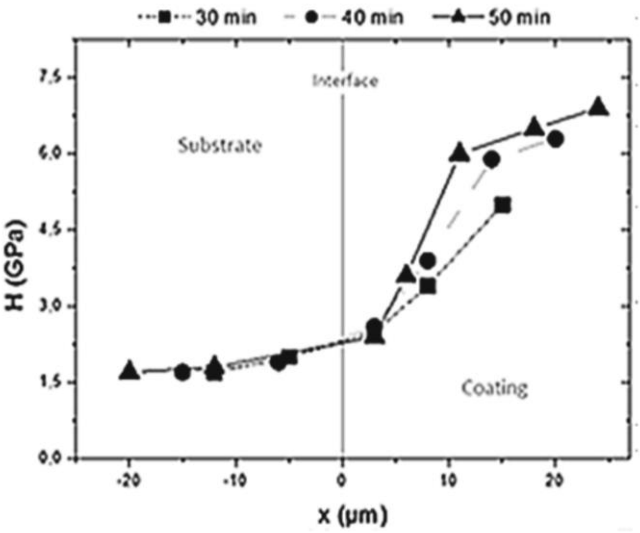

Fig. 6. Hardness-depth profile of cross section of samples for three immersion times

This figure reveals three different areas. The first one corresponding to the steel substrate, the hardness takes smallest values estimated to 1.6 GPa. Close to the interface and into the coating, there is a second area. It appears that the hardness of chromium coating increases with the profile distance. The third zone shows the high and stationary hardness values which correspond to chromium coating. For different immersion times, the hardness of the chromium layer in the interfacial region takes a value in the order of 2.7 GPa. In this case, the steel substrate has an influence on the hardness of the chromium layer.

For immersion times of 30 and 50 min, it is shown that the hardness of chromium coating respectively takes the values of 4.6 and 8.4 GPa. This characterization allows for confirming the thickness of chromium coating observed optically by using metallographic analysis.

4 Conclusions

Hard chromium, obtained by electroplating, is considered one of the most interesting coating materials, possessing excellent mechanical and chemical properties against wear and corrosion. Among the existing technological parameters relating to this subject, we selected immersion time as the only parameter in this study. The immersion time effect on the mechanical and microstructural properties of produced coatings was reported. The formation of the chrome layer was confirmed by XRD analysis. As showed the micrographs of the cross section of the samples, the thick chromium coating increases with the increasing immersion soaking time. The growth rate of produced coating depends on the stacking of chromium charges of the electrolytic solution deposed on the steel substrate. The growth of the chromium coating in our case is governed much more by the diffusion process than the precipitation process which is the longest. For this reason, the coating is found in an unstable state causing internal stresses which contribute to the observed hardening.

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