

A Surface Conversion Treatment on a Borided and Cemented Steel Coated with Chromium Filme

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Abstract: Coatings based on chromium borides and chromium carbides are commonly employed in applications requiring high hardness, low friction coefficient, as well as corrosion resistance. In this work, we made layers of chromium borides and chromium carbides on the surface of low carbon steel through some specific treatments. For chromium borides, the boriding treatment in a solid medium at 900°C for 4 h was followed by chromium electroplating on the steel surface and finally the application of annealing treatment at 950°C for 1 and 2 h. For chromium carbides, the cementation in a solid medium was followed by electroplating of chromium on the surface and finally the application of annealing treatment in the temperature range between 500 and 1100°C for 1 h. The results showed that, in the first case, boron diffusion and chromium deposition led to chromium borides on the treated surface. Similarly, for the second case, the cemented layer and the chromium deposited on the surface combined to form chromium carbides on the treated surface after annealing. The characteristics of the chromium borides and chromium carbides obtained were very similar to those of chromium borides and chromium carbides obtained by other processes.

Keywords: Chromium, deposition, steel, layer, diffusion, cementation, boriding, annealing.

1. INTRODUCTION

One of the major causes of the degradation of materials comes from the interactions of their surface with the surrounding environment: mechanical and thermal interactions responsible for wear or fatigue cracking phenomena, chemical interactions at the origin of corrosion phenomena. It is therefore absolutely imperative to take them into account to reduce maintenance costs in industrial equipment. Furthermore, oxidation or loss of adhesion in the case of assemblies is very closely linked to the roughness, the state of residual stresses, and the metallurgical structure of the surface [1-3].

It is very rare that the surface of a material, as it results from processing, hot or cold processing, heat treatments, or finishing, satisfies all the properties required in the field of use. The aim of surface treatments and coatings is therefore to allow the metallic material to be suitable for the requested functions [4-6].

In recent years, the thin layers of carbides, borides, and nitrides of transition metals obtained

by various methods have been widely studied. Chromium borides and chromium carbides are distinguished by better hardness and good resistance to wear and corrosion with regard to several aggressive media [7-9].

It quickly emerged from these studies that the films deposited can improve the surface layers of the materials with respect either to an increase in hardness, or to a reduction in friction of the parts in contact, or even to protect against wear and corrosion [10-12].

The importance of the properties of borides and chromium carbides prompted us to study the possibility of producing these borides and carbides by conversion treatments based on the electroplating of chromium and the diffusion of carbon and boron [13, 14].

The objective of this work is to produce chromium borides and chromium carbides layers on a low alloy steel substrate by double surface treatment (increasing the boron and carbon content at the surface of the substrate using a standard process (boriding and cementation) + electrolytic deposition of chromium layer +

annealing which would allow the diffusion of boron and carbon toward the surface of the material to combine with chromium to form chromium borides and chromium carbides throughout the coating) with the chemical, microstructural and mechanical characterization of the coatings obtained.

2. EXPERIMENTAL PROCEDURES

2.1. Materials and coating deposition

The chemical composition of the steel (16Mn₂) substrate (Table 1) was determined by spectrometric analysis, using an arc-type spectrometer of HT in argon. The initial hardness of the substrate is 320 HV.

To conduct a comparative study, we divided the samples into 02 groups:

- Samples preparation, boriding, coating with a chromium layer, heat treatment, characterization of obtained deposits.
- Samples preparation, cementation, coating with a chromium layer, annealing at temperatures between 500 and 1100°C for 1 h, characterization of obtained deposits.

The preparation of the substrate consists of a mechanical polishing on each sample using abrasive papers. The finishing operation provides a good polishing with felt washed down with a suspension of alumina in water. The polished surface must be cleaned thoroughly with water and dried with compressed air and hot filtered.

The boriding treatments were performed in an electric muffle furnace. The samples to be boronised are placed in an ordinary steel crucible with a lid. For the good efficiency of the boriding powder, the crucible cover was concealed by a clay paste. To ensure a good homogenization of cement throughout the volume, it is stirred for several minutes. The boriding treatment was conducted for a period of 4 hours at a temperature

of 900°C. This treatment provides a boron-treated layer with a thickness of approximately 150 µm.

Cementation is performed using a cement coke powder at a temperature of 900°C for 6 h, to accelerate cementing, barium carbonates BaCO₃ is added to coal activators. With this method, a carburizing depth of 1.3 mm was obtained.

Samples were chrome electroplating, the standard composition of plating bath: 250 g/l CrO₃, 2.5 g/l SO₄H₂, bath temperature (40- 44°C), antimony lead anode, retention time 1/2 hours and deposition rate of about 40 µm/h.

To obtain a layer of chromium boride layer, samples were a thermal annealing treatment at the temperature of 950°C for 1 and 2 h.

For chromium carbide, chromium-coated samples were a thermal annealing treatment in the temperature range (500-1100°C). The hold time is equal to 1 h.

2.2. Characterization and analysis techniques

Microscopic observation requires fine polishing of the surface to be observed. Cleaning with acetone and drying by hot airflow. The second phase consists of a chemical attack using the product nital. For microscopic observations, the apparatus used is a universal optical metallographic LEICA type microscope (DMLM) allowing the observation of the samples, with an enlargement that varies from 50 to 1000.

The morphology of the deposits was also examined with a TESCAN VEGA scanning electron microscope. The acceleration voltage used for secondary electron observations was most often at 15 and 25 kV, and the probe current 75 to 160 mA. Most of the samples were glued to the sample holder with graphite glue and metalized with silver to facilitate analysis.

X-ray diffraction analysis was performed to determine the phases at the sample surface using an RX D8 Advance Bruker diffractometer.

Table 1. Chemical composition of steel to be coated (%)

| Fe | C | Si | Mn | P | S | Cr | Mo | |
|-------|-------|-------|-------|-------|--------|-------|-------|-------|
| 98.3 | 0.16 | 0.076 | 0.516 | 0.01 | 0.014 | 0.147 | 0.005 | |
| Ni | Al | Co | Cu | Nb | Ti | V | W | Sn |
| 0.126 | 0.065 | 0.05 | 0.55 | 0.006 | 0.0015 | 0.005 | 0.05 | 0.062 |

The hardness profile of the samples was measured along the cross-sections using a micro-indenter type Wilson Hardness (TUKONTM 2500).

Three Vickers indentations using a load of 20 grams for 15 s were performed at each depth to obtain a significant statistical value.

3. RESULTS AND DISCUSSION

3.1. Morphology

The observation of the cut layer/substrate sections of the treated samples shows the formation of multilayers from the surface towards the core of the substrate. The microstructure of these layers

is very variable: it is fibrous in unidirectional columns for the outer layer and without any preferential orientation for the second layer and the transition zone. Note that the initial microstructure of the chromium deposit was mainly made up of platelets on the surface of the substrate. Recall that this kind of morphology occurs in several cases of phase change in the solid-state [6, 21]. Increasing the amount of diffusing boron on the substrate causes a progressive spread of chromium boride in the chromium deposit (Fig. 1). When the coated substrates are annealed for two h (Fig. 2), the chromium matrix is completely converted to chromium borides.

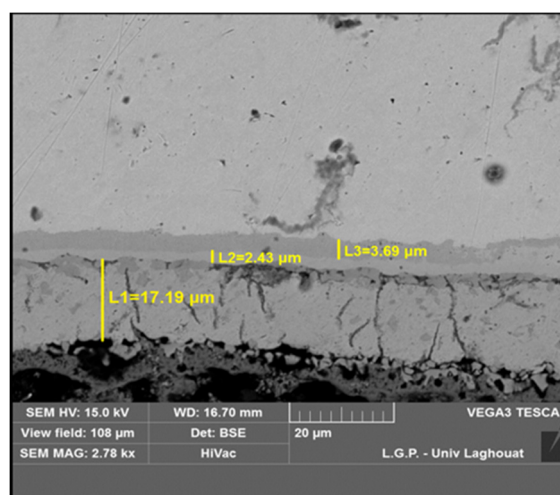
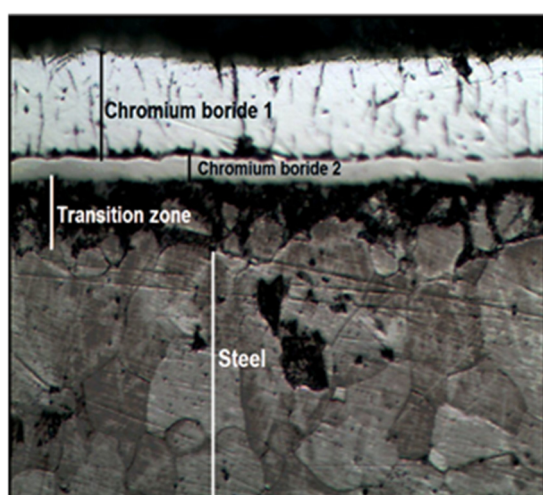


Fig. 1. Observation of metallographic faces layer/substrate of the sample having undergone boriding followed by chromium deposition after one hour annealing.

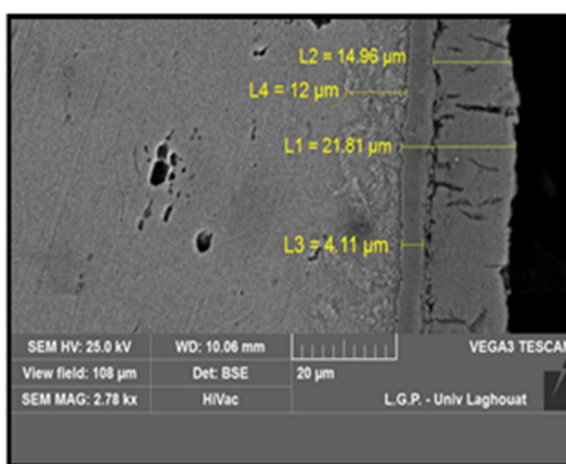
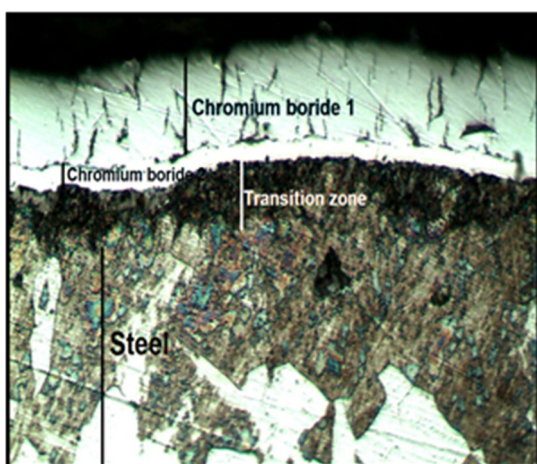


Fig. 2. Observation of metallographic faces layer/substrate of the sample having undergone boriding followed by chromium deposition after two hours of annealing.

Micrographs of polished and etched cross-sections of the coated samples are shown in Fig. 3 where the outer chromium film (in white) is visible (Fig. 3(a)). A thickness of $\sim 20\ \mu\text{m}$ can be estimated for the as-deposited or annealed specimen at low temperature. At the intermediate temperature of 700°C and 1000°C as shown in Fig. 3 (b, c, d, e), three different regions were observed (I) the outer layer composed of

chromium, (II) the inner layer composed of a mixture of chromium carbide phases and (III) the cemented steel substrate. At 1100°C , the chromium film is completely transformed into chromium carbide (Fig. 3(f)). These observations confirm that the precipitation begins at the interface substrate-film and progresses toward the surface as the treatment temperature increases [15, 16, 20].

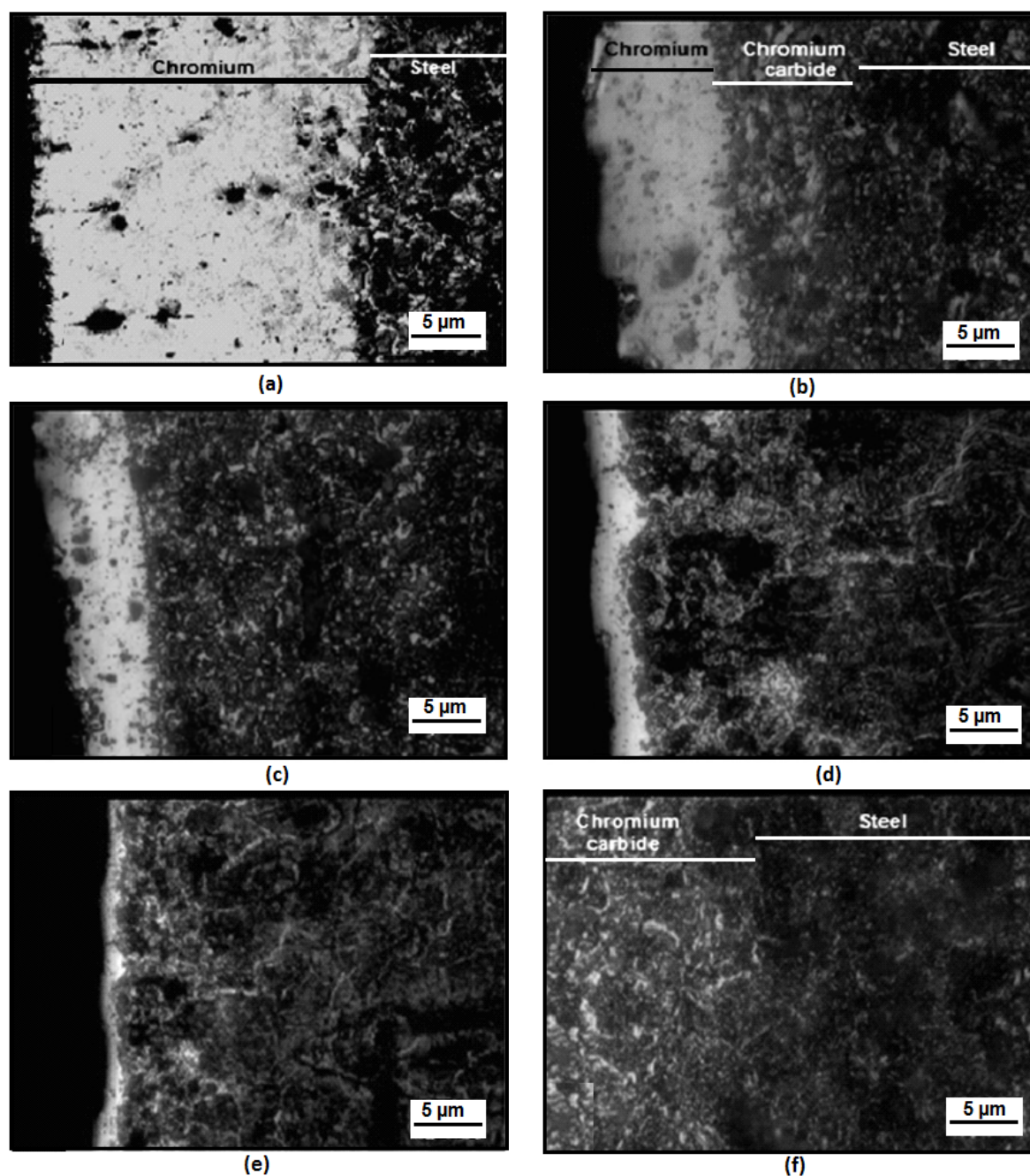


Fig. 3. Optical photographs of chromium deposited on cemented steel as-deposited (a), annealed at 700°C (b), at 800°C (c), at 900°C (d), at 1000°C (e), and at 1100°C (f).

When the coated substrates are annealed for two hours, the chromium matrix is completely transformed into chromium carbides and borides. The layer formed has an almost granular structure. The morphology of chromium carbide and boride deposits depends mainly on the annealing time which promotes the mobility of atoms in the layer and the substrate. This mobility promotes the diffusing path of the element carbon and boron in high concentration from the substrate to the layer. We note that the contribution of the thickness of the carburizing and boriding zone is minimal in terms of the transformation of the chromium layer into chromium carbide and boride. Compared to the total thickness of the deposit, the thickness of the transformed layer has ratios that correspond respectively to the annealing time of one hour and two hours. Generally in our case, it is the high treatment temperature that plays an essential role in the transformation of the chromium layer deposited into chromium carbide and boride.

3.2. Structure

Fig. 4 (a) shows the x-ray diffraction spectrum for the sample (Boriding + chromium plating) after one-hour annealing. The diffractogram shows different diffraction peaks relating to chromium boride Cr_2B , iron boride Fe_2B , iron oxide Fe_2O_3 , chromium oxide Cr_2O_3 , and a small amount of chromium Cr.

Fig. 4 (b) shows the x-ray diffraction spectrum for the sample (boriding + chromium plating) after two hours of annealing. The diffraction spectrum corresponds to the sample having peaks relating

to chromium boride Cr_2B , iron boride Fe_2B , iron oxide Fe_2O_3 , and chromium oxide Cr_2O_3 having a high diffraction intensity.

For an annealing time of one hour, we notice in this case that the boron of the boriding zone begins to diffuse in the chromium layer deposited from the layer/substrate interface [14-18]. When the annealing retention time is high (after annealing of two hours), the chromium peak disappears completely and the peaks corresponding to the chromium borides appear relatively at high intensities, the chromium oxide and iron oxide phases are inevitable, this is due to the oxidizing atmosphere of the oven [17, 19]. X-ray diffraction examination of the samples did not reveal the presence of chromium. This leads us to say that the growth of the precipitated phase of chromium boride reaches the outer layer of the deposit. The iron atoms diffusing in the layer take a very weak range; this is why there is no peak corresponding to this element in the diffractograms. The deposited chromium is completely transformed into chromium borides [12, 17].

Fig. 5 presents the X-ray spectra of chromium layers as-deposited and treated at an annealing temperature of 500°C , 800°C , and 1100°C . For the untreated sample, the film is primarily composed of chromium. The chromium layer treated at an annealing temperature of 500°C reveals almost the same structural character as-deposited chromium. For this temperature of treatment, no precipitation of chromium carbide phase was observed apart from the presence of chromium oxide characterized by a peak of low intensity.



Fig. 4. X-ray diffraction pattern chromium film on borated steel after one hour annealing (a) and after two hours of annealing (b).

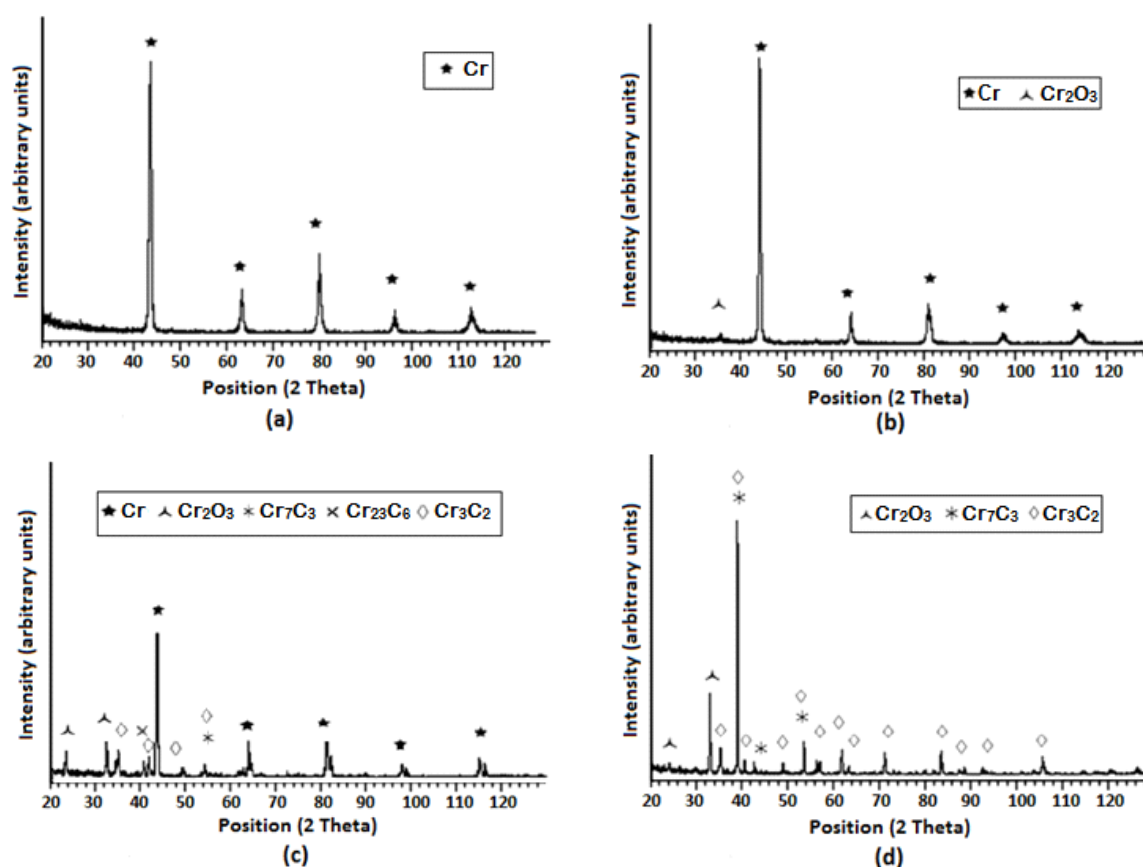


Fig. 5. X-ray diffraction pattern chromium film on cemented steel substrate as-deposited (a), annealed at 500°C (b), at 800°C (c), and at 1100°C (d).

The presence of Cr_2O_3 at the surface of the samples is due to the reaction between the chromium layer and the oxygen present in the atmosphere of the furnace. The formation of the chromium oxide phase can be explained by the low free energy of formation (-570 KJ/mol). Chromium carbide starts to be formed by carbon diffusion from the carburized zone of the steel substrate just before 800°C.

The gradual formation of this new phase increases with the tested temperatures from 800°C to 1100°C. For these temperatures, two separate layers are observed in the films. The outer region composed of pure chromium where the transformation has not started since the carbon has yet not reached this zone and the inner region where carbide precipitation has already started. Three different phases of chromium carbide: Cr_{23}C_6 , Cr_7C_3 , and Cr_3C_2 can be identified in the coating. For the annealing temperature of 1100°C, complete conversion of the chromium film in chromium carbides is obtained, this result is achieved by Ganguly, A. et al [15], and Music, D. et al [16].

3.3. Hardness

Micro-hardness measurements at 20 g load were made on different areas of the formed layer on the surface. The values of the micro-hardness depending on different areas and depending on the treatment carried out are in Tables 2 and 3.

For samples of (boriding + chromium), for 1h annealing, the micro-hardness of the deposited layers increases. It may be thought that in this annealing domain, the flow of boron atoms from the substrate (boriding layer) is high. A greater amount of chromium boride created later would be responsible for the hardening observed. After two hours of annealing. The hardening would therefore be related to the complete formation of chromium boride which would cause a strengthening of the deposits [8, 19].

For samples of (cementation + chromium), the changes that are observed in the hardness gradient can be related to the carbon potential at the interface between the carburized material and the chromium layer.

Table 2. Microhardness recorded on different areas of the surface for samples (boriding + chromium).

| | Zone A | Zone B | Zone C | Zone D |
|---------------------------|--------|--------|--------|--------|
| After annealing one hour | 1880 | 1310 | 369 | |
| After annealing two hours | 2615 | 2110 | 847 | 389 |

Table 3. Variation of the micro-hardness as a function of the temperature for samples (cementation + chromium).

| Temperature (°C) | Without annealing | 500 | 700 | 900 | 1100 |
|---------------------|-------------------|-----|------|------|------|
| Micro-hardness (HV) | 965 | 835 | 1060 | 1580 | 2110 |

At 500°C there is no observable increase in hardness in accordance with the X-ray measurements that show no carbide precipitation. The hardness, 835 HV, is only that of the chromium phase. At 700°C, carbon is provided only from ferrite since the Fe_3C is still stable at this temperature and the hardness is limited to 1060 HV at the interface. At 900°C on the contrary, the carburized material, near the interface, is only composed of austenite of much higher carbon solubility, near 1%, thus increasing the quantity and level of carbon available for diffusion. Hardness reaches 1580 HV for this temperature. At 1100°C the process of diffusion is increased in proportion. The chromium is completely transformed over the whole layer and the hardness of 2110 HV is only that of the carbide. These values are in accordance with that mentioned in [9, 15, 16] for Cr_3C_2 and Cr_7C_3 carbides.

4. CONCLUSIONS

Using different annealing treatments performed on chromium films deposited by an electrolytic process on borided and cemented steel substrates, it was possible to totally transform the chromium film into chromium boride and chromium carbide by using only boron carbon atoms coming from the borided and cemented zone of the steel substrate. For group 1 samples (carburizing + chromium), it was noted that in the annealing temperature of 500°C, thin films retain their monophasic character. They almost kept the same hardness values as the control sample. It should be noted that in the temperature range between 700 to 900°C the incipient phase that appears at 700°C is increased while the amount of chromium phase decreased. This caused hardening of the obtained deposit. After annealing at 1100°C, the

chromium layer was completely converted into chromium carbides that is responsible for the increase in the hardness values. For Group 2 samples (boriding + chromium) and for an annealing time of one hr, it was noticed that the boron in the boriding zone diffused into the chromium layer deposited from the layer/substrate interface. When the annealing time was high (after two hrs of annealing), the chromium layer was completely transformed into chromium boride. The results obtained using the new methodology proposed in the present work show that very simple and widespread technologies such as carburizing and boriding, electrolytic coating, and thermal treatment can lead to very hard and resistant coatings.

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