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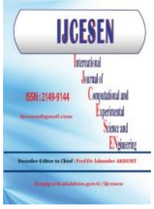

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Research Article

Effect of the annealing temperature and the thickness of carburizing layer on the obtained chromium carbides#

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Abstract: Low carbon steel substrates were surface hardened by carburizing in solid medium, and then thin layers of chromium were deposited by electrolytic way. After chromium deposition, the samples were exposed to isothermal annealing at temperatures between 500 and 1100 °C for 1 and 2 hours duration. The obtained thin layers were characterized by X-rays diffraction, optical microscopy and Vickers micro-hardness.

The obtained results showed that chromium layers are transformed into chromium carbide by metastable phases of transition. At 500 °C annealing temperature thin films retain their monophasic character Crα, and they almost keep the same hardness values. When temperature range is between 700 and 900 °C the incipient phase appears and is increased while the chromium mother phases decrease. After annealing at 1100 °C, the chromium layer is completely converted into chromium carbides that would be responsible for the increase of the hardness and adhesion layer / substrate.

1. Introduction

Recent research on chromium carbide stressed their resistance to oxidation and corrosion and suggested that they have great potential to replace hard chrome electroplating as protective coatings [1, 2]. The chromium carbide layers can be obtained by physical vapor deposition (PVD) [3, 4] or thermo-reactive deposition/diffusion (TRD) technology [5, 6]. In the case of PVD thickness is much less than 10 µm making those unfit also withstood the high contact pressure and further adhesion to the substrate is less than that obtained with other types of coating techniques [7, 8]. TRD coatings must very long process times at high temperatures. Indeed, there are very common industrial methods that can be combined in any manner to produce chromium carbide coatings [9, 10].

In order to produce a high-hardness coating, a good adhesive properties and a sufficient thickness with stand severe loading conditions, we propose an alternative technique based on a three-step process using only standard industrial methods. The first step intends to increase the carbon content at the surface of the substrate using a standard carburizing process. The second step consists to coat the carburized material with a layer of chromium. The final step considers the heat treatment at temperatures which allow the diffusion of carbon into the surface of the material. In this work, we propose to determine the experimental conditions which allow complete conversion of the chromium layer in a uniform layer of high hardness of chromium carbide and a good adhesion to the substrate.

2. Experimental methods

2.1. Materials and coating deposition

Cylindrical samples were selected of 20 mm in diameter and 15 mm length. The chemical composition of the substrate was determined by spectrometric analysis using a spectrometer HILGER. The preparation of the substrate consists on a mechanical polishing on each sample using abrasive papers.

Table 1.*Chemical composition of the steel to be coated*

Fe	**C**	**Si**	**Mn**	**P**	**S**	**Cr**
95.99	0.19	0.22	0.94	0.003	0.056	1.12
Mo	**Ni**	**Al**	**Co**	**Cu**	**Ti**	**Sn**
0.07	1.18	0.0116	0.01	0.20	0.0012	0.010

This 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.

Carburizing is performed using a cement coke powder at temperature of 900 °C, to accelerate cementing, barium carbonates $BaCO_3$ is added to coal activators. The carburizing thickness obtained are (E_1= 00 mm, E_2= 0.6 mm, E_3= 1.3 mm and E_4= 2.5 mm).

Samples were chrome electroplating. Retention time ½ hours and deposition rate of about 40 µm/h. In order to obtain a layer of chromium carbide, chromium coated samples were a thermal annealing treatment in the temperature range (500-1100 °C). The hold time is equal to 1 hour.

2.2. Characterization and technics analysis

Microscopic observation requires fine polishing of the surface to be observed. Cleaning with acetone and drying by hot air flow. The second phase consists of a chemical attack using the product nital. The equipment used is a universal optical metallographic microscope ZEISS type. Cemented steel area, thickness of chromium layers deposited and annealed was measured by an optical micrometer associated to the optical microscope.

X-ray diffraction analysis was performed to determine the phases at the sample surface using a PHILIPS X'PERT PDM diffractometer.

The hardness profile of the samples was measured along the cross-sections using a microdurometer type Buehler MICROMET (HARDNESS TESTER). Five Vickers indentations using a load of 50 g were performed at each depth in order to obtain a significant statistical value.

3. Results and discussion

3.1. Microstructure

At the temperature of 500 °C, the X-ray diffraction analysis did not detect alterations in the thin layers of chrome deposited on steel substrates treated by cementation for four periods of carburization. Diffraction patterns are similar to that on the sample which has not undergone thermal treatment.

At the temperature of 700 °C the diffraction patterns of X-rays show transformation start of chromium phase to chromium carbide. The diffractogram corresponding to the sample E1 = 00 mm has different diffraction peaks relative to the iron, chromium and chromium oxide. The revelation of this last phase in this deposit probably reflects contamination of the chromium layer by the surrounding atmosphere. The annealing treatment is performed in a furnace in the absence of vacuum. This facilitates on the one hand the formation of chromium oxide. The low energy of formation of chromium oxide relative to chromium carbide translated other hand the presence of the Cr_2O_3 phase in the deposit. For samples E_2 = 0.6 mm and E_3 = 1.3 mm, phases detected in the diffraction patterns are recorded: Cr, Cr_{23} C_6, (Cr, Fe) $_{23}$ C_6 and a small amount of Cr_2 O_3. In this case it has been noted that the carbon of the carburizing zone begins to diffuse into the chromium layer deposited from the interface layer / substrate. The diffraction pattern corresponds to the sample E_4 = 2.5 mm showing peaks related to chromium, chromium carbide Cr_{23} C_6 and chromium oxide Cr_2 O_3, which exhibited a weak diffraction intensity. In the annealing treatment step, the flow of carbon diffused carburizing zone to the layer is high. This fact is due to great thickness of carburizing which contains carbon content in excess.

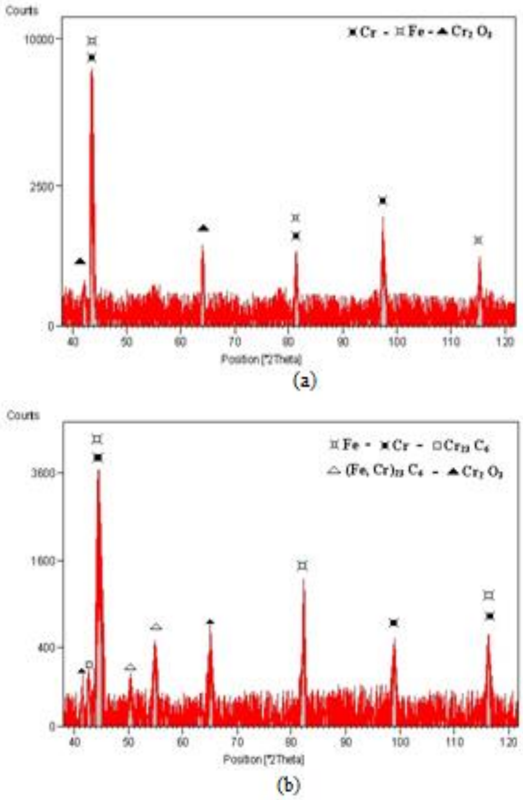


Figure 1. *X-ray diffraction spectra after annealing at 700 °C of: (a) sample E_1 = 00 mm, (b) sample E_3 = 1.3 mm.*

At the temperature of 900 °C, the rate of transformation of chrome to chromium carbide increases sharply. This is reflected in the intensity of the diffracted peaks of different phases composing the layers formed. For sample $E_1 = 00$ mm, it has been noted an increase of chromium oxide (Cr_2O_3), a decrease of Cr and the formation of Fe_2O_3. The diffractograms of samples $E_2 = 0.6$ mm and $E_3 = 1.3$ mm show the phases of Cr_2O_3, $Cr_{23}C_6$, $(Cr, Fe)_{23}C_6$ and a low proportion of Cr. A second chromium carbide phase Cr_7C_3 appeared. When the thickness of the carburized layer is higher ($E_4 = 2.5$ mm), chromium peak completely disappears and the peaks corresponding to chromium carbides ($Cr_{23}C_6$, Cr_7C_3) appear relatively large currents. For high process temperatures, the chromium oxide layer is unavoidable. This fact is due to the oxidizing furnace atmosphere.

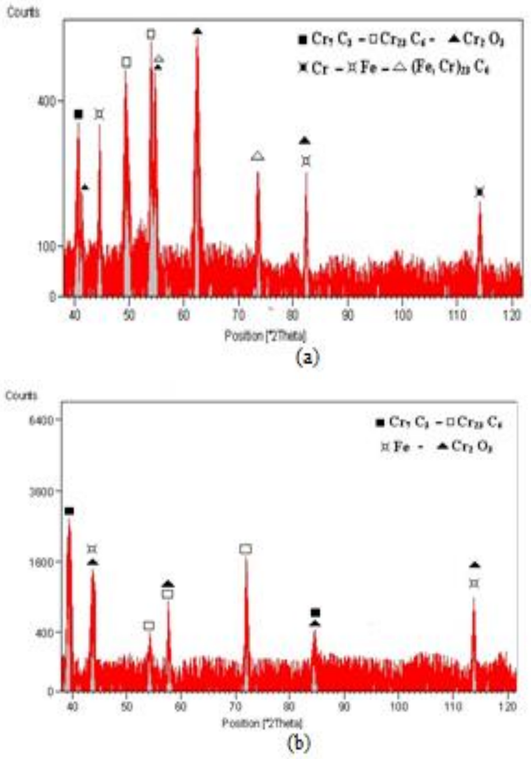


Figure 2. *X-ray diffraction spectra after annealing at 900 °C: (a) sample $E_3 = 1.3$ mm, (b) sample $E_4 = 2.5$ mm.*

For greater processing temperature used (1100 °C), the deposited chromium is completely converted into chromium carbides. Examination by X-ray diffraction of the samples E_2, E_3 and E_4 does not reveal the presence of chromium. This leads us to say that the growth of the precipitated chromium carbide phase reaches the outer layer of the deposit. Phases recorded for samples E_2 and E_3 are: $Cr_{23}C_6$, Cr_7C_3, Cr_2O_3 and $(Cr, Fe)_{23}C_6$. The sample E4 this in its phases layer: $Cr_{23}C_6$, C_3Cr_7 and Cr_2O_3. For non-cemented sample, the recorded phases are: Cr, Cr_2O_3 and Fe_2O_3. In this case, it is both the thicknesses of the layers of carburization and high temperature treatment which play an essential role in the transformation of the chromium layer to chromium carbides.

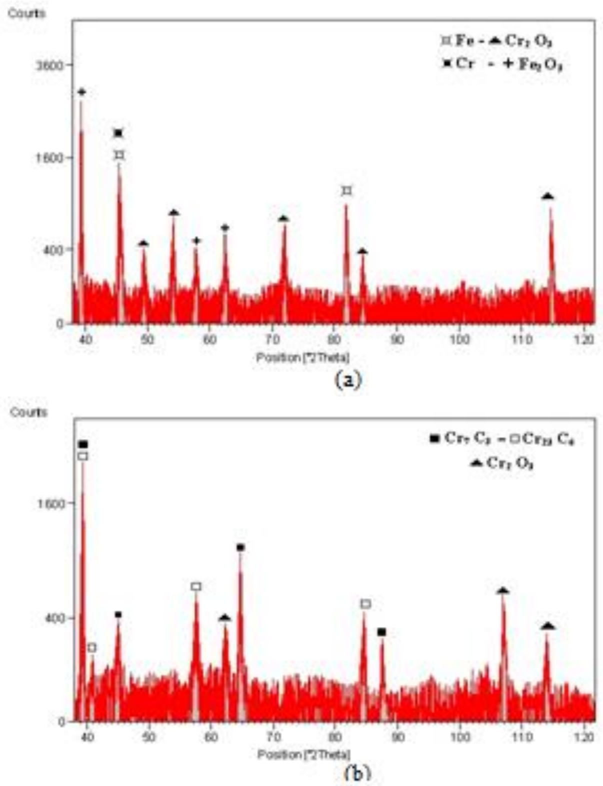


Figure 3. *X-ray diffraction spectra after annealing at 1100 °C: (a) sample E1 = 00 mm, (b) sample E4 = 2.5 mm.*

3.2. Morphology

The four samples annealed at 500 °C, no chromium carbide trace could be revealed same for the samples without cementation.

After treating the sample $E_2 = 0.6$ mm at 700 °C by annealing, a chromium carbide edge occurs in the vicinity of the interface. This is reflected by the low diffusion of carbon cementation zone in the deposited chromium layer. For the sample $E_3 = 1.3$ mm, the resulting layer always keeps the same structure. The latter appears more clearly in the photograph corresponding to the sample $E_4 = 2.5$ mm. The thickness of the carburized layer of the substrate presents a great effect on the chromium conversion rate chromium carbide. Observation of faces layer/substrate treated at 900 °C reveals fibrous structures in the unidirectional columns. In the picture corresponding to the sample $E_4 = 2.5$ mm, it has been noted that the microstructure is predominantly in chips arranged on the substrate surface. This kind of morphology is found in several cases of phase change in the solid state. The structure of the incipient phase is usually in the form of needles certain plane oriented parallel to the surrounding parent phase. Increasing the

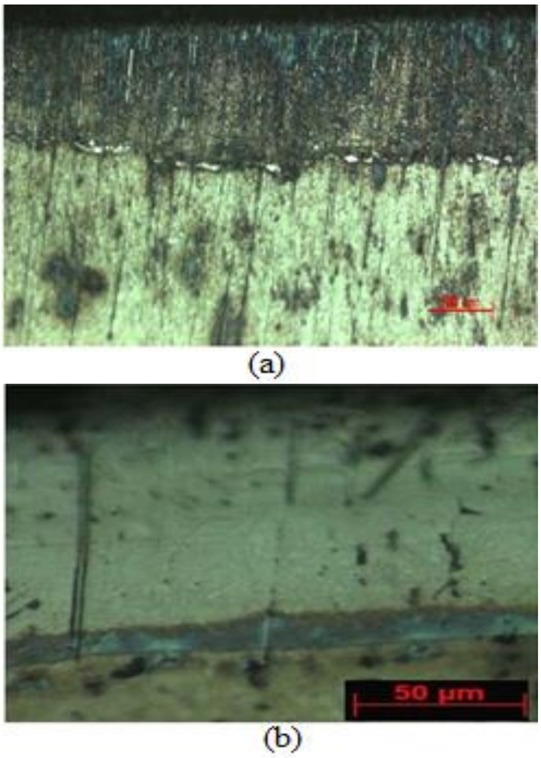
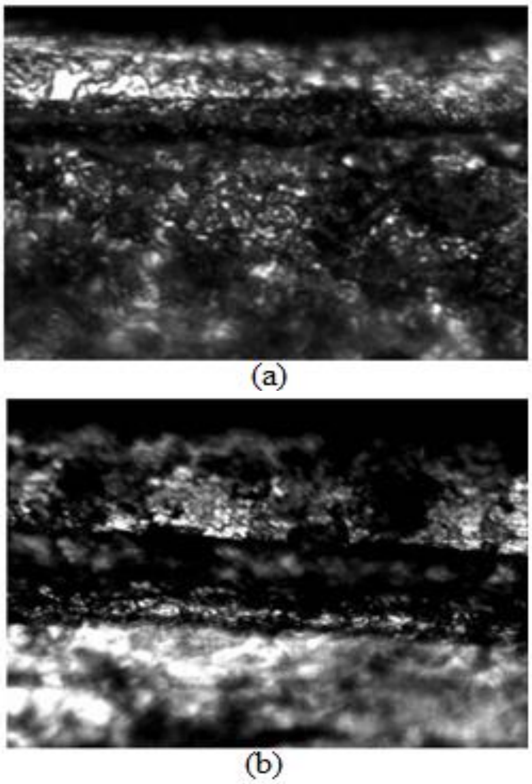


Figure 4. *Metallographic observation of layer/substrate interface after annealing at 700 °C: (a) sample* E_3 *= 1.3mm, (b) sample* E_4 *= 2.5mm.*

amount of carbon diffusion from the substrate causes a progressive propagation of chromium carbide in the deposition of chromium. When the coated substrates are subjected to annealing at 1100 °C, the chromium matrix is transformed completely to chromium carbides.



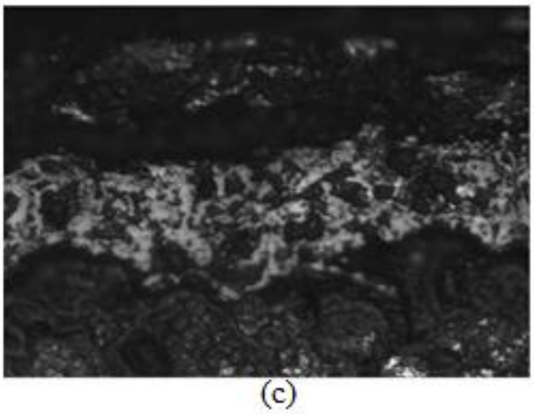


Figure 5. *Metallographic observation of layer/substrate interface after annealing at 900 °C: (a) sample* E_2 *= 0.6 mm, (b) sample* E_3 *= 1.3 mm, (c) sample* E_4 *= 2.5 mm.*

The morphology of the deposit of chromium carbides mainly depends on the treatment temperature, which promotes the mobility of atoms in the layer and the substrate. Mobility supports traverses the diffusing carbon element concentration from the substrate to the layer. Indeed, the thickness of the carburized layer presents a great effect on the chromium conversion rate into chromium carbides.

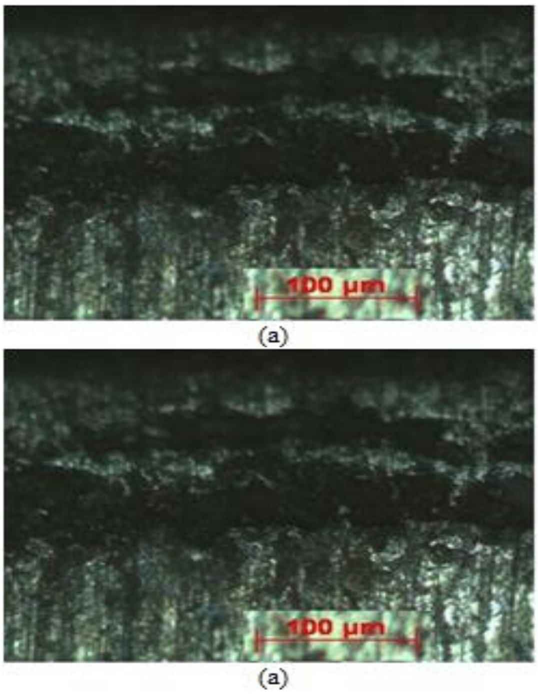


Figure 6. *Observation of metallographic faces layer/substrate after annealing at 1100 °C: (a) the sample* E_2 *= 0.6 mm, (b) the sample* E_4 *= 2.5 mm.*

3.3. Hardness

Figure 7 shows the effect of Annealing temperature on the micro-hardness. According to these results, it is clear that the micro-hardness of the deposited layer is gross larger than processed at low temperatures. This may be due to the fact that the chromium layer is not in its most stable state and present stresses caused by the incorporation of impurities during the deposition step.

Micro-hardness of thin films annealed at 700 °C shows relatively small increases. This may be due mainly to the phase change. This small increase can be explained by a very low carbon diffusion of the substrate (carburizing layer) that could be detected by the used analysis method.

For annealing temperature at 900 °C, the micro-hardness of the deposited layers increases rapidly. In this temperature range, the flow of carbon atoms from the substrate (carburizing layer) is high. A greater amount of chromium carbide created thereafter would be responsible hardening observed. The grain growth of the layer and the long range diffusion of substrate carbon atoms are two competitive processes that would probably influence the micro-hardness in the preceding temperature.

For the annealing temperature 1100 °C, micro-hardness still is evolving in ascending order. Micro-hardness measurements made on samples E_3 and E_4 show that the micro-hardness is even greater than that of the sample E_2. Curing would be linked to the complete formation of the chromium carbide that will cause a reinforcing of deposits. From these results, we can confirm that the difference between the cementation thicknesses may cause difference in micro-hardness.

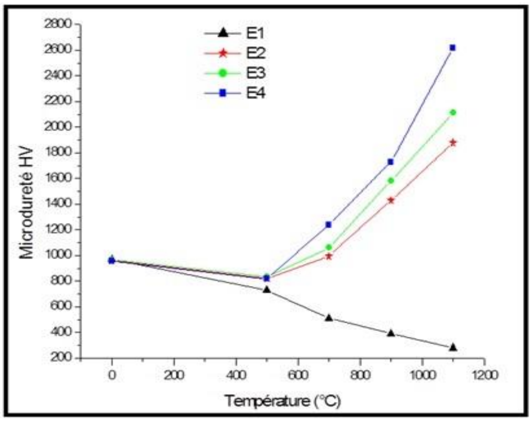


Figure 7. *Annealing effect on the micro-hardness of the deposited layer.*

4. Conclusion

In this paper, we are interested on the increasing of the performance steels chromium carbide creation with high features. For thus and after carburizing and deposition by electroplating, a chromium layer on the steel samples (layer / substrate) were subjected to annealing in the range (500-1100 °C). In this temperature range, the deposited film is gradually converted to chromium carbide. Phase transformation which took place primarily by diffusion of the substrate of carbon atoms in the layer was determined by x-ray diffraction and metallographic analysis. The hardness of the produced layers evolved following the annealing temperatures and the thickness of carburized layer. The obtained value is in agreement with the changing properties determined by the x-ray diffraction and microscopic observation.

Indeed, it has been noted that the annealing temperature 500 °C, thin films retain their monophasic character Crα, they almost keep the same hardness values than the control sample. It should be noted that in the temperature range 700 to 900 °C the incipient phase that appears at 700 °C is increased while the chromium mother phase undergoes a decrease. This causes a high hardening of the obtained deposit. After annealing at 1100 °C, the chromium layer is completely converted into chromium carbides that would be responsible for the increase of the hardness and adhesion layer / substrate.

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