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PROCESSING CONDITIONS INFLUENCE ON THE CARBOCHROMIZED LAYERS ON SINTERED IRON MATRICES

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În lucrare sunt luate în analiză efectele variației parametrilor tipici ai celor două tratamente termochimice, carburare, respectiv cromizare, asupra compoziției fazice a straturilor carbocromizate obținute pe matrici de fier sinterizate. Utilizarea carbocromizării pentru durificarea produselor metalice poate asigura pe lângă o creştere considerabilă a caracteristicilor de rezistență mecanică a straturilor superficiale şi o majorare substanțială a rezistenței la coroziune, respectiv eroziune, la temperatură ambiantă sau ridicată. Matricile procesate prin metode specifice metalurgiei pulberilor, la densități apropiate de ale materialelor compacte (porozitate închisă sub 10%) au o comportare la tratament termochimic similară sau superioară celor obținute prin procedeele clasice de procesare, cinetica formării straturilor fiind frecvent superioară celei înregistrate la materialele tradiționale. Compoziția fazică a straturilor carbocromizate este strict dependentă de parametrii termici şi temporali ai celor două tratamente termochimice şi nu în ultimul rând de cei chimici ai acestora.

In this paper we will analyze the effects of the thermochemical processes parameters variation on the carbochromized layers obtained on sintered iron matrices. The use of carbochromizing for hardening of metallic products provides, besides a considerable increase of the mechanical characteristics of the superficial layers, an improvement of the anticorrosion and anti erosion characteristic properties both at room temperature and high temperatures. The matrices obtained by specific techniques of powder metallurgy have density values close to those of the compact materials (i.e. porosity below 10%) and possess similar and sometimes improved properties in exploitation with respect to those of materials obtained through classic techniques. This happens due to the kinetics of the layer's formation that is frequently superior to those developed during the preparation of the classic materials. The phase composition of the carbochromized layers is strictly dependent on the thermal, temporal and chemical parameters of the two mentioned thermochemical processes.

Keywords: iron matrices, powder metallurgy, carbochromizing

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1. Introduction

The search of new coatings meant to improve the materials resistance to different mechanical stresses has always been a challenge in material science [1, 2]. Among these materials Fe-Cr-C alloys are used in severe conditions to prevent erosion where large abrasion resistance is necessary [3-5]. Although their hardness is lower than that of vanadium or tungsten carbides, chromium carbides obtained during the preparation of Fe-Cr-C have a much better high temperature oxidation resistance up to 700^{o}C [6]. In many cases, obtaining Fe-Cr-C coatings was achieved by diffusing Cr into Fe-C or steel with C content lower than 1% [7]. Due to the limited diffusivity of chromium at low temperatures, the conventional chromizing processes are usually carried out at temperatures around 1000^{o}C and during 6 to 10 hours [7, 8]. The investigation of Fe-Cr-C alloy microstructures has shown that these types of materials have hypoeutectic, eutectic and hypereutectic structures [9]. Studies have revealed that the layers obtained by carburising followed by chromizing consisted mostly of carbides with the following stoechiometry: $M_{23}C_6$, M_7C_3, M_3C_2 [4, 5, 7, 10]. However, the Fe-Cr-C layer properties depend strongly upon the synthesis technique and the parameters (such as temperature, time, and atmosphere) of the thermochemical treatment.

2. Experimental details

In order to highlight the phase composition of the carbochromized layers obtained on iron matrices and the effects of the variation of the parameters of the thermochemical treatments, experimental researches were carried out using iron powder. The powder was obtained by water pulverization followed by the Höganäs reduction method, on 16 mm in diameter and 11 mm thick samples, made by pressing (735 MPa) and then sintering at 1000^{o}C, for 4 hours in neutral atmosphere (nitrogen). In these conditions the resulting samples presented a porosity of 8 to 10%. Due to the multitude of technological parameters of the termochemical treatments, carburising and chromizing, and due to the necessity of quantifying the individual and collective influences of these parameters on the phase composition of the obtained carbochromized layers, the programming experiments method was imposed. The chosen method was the orthogonal central compositional program of the second order [11], the parameters taken into consideration and the variation intervals of these parameters being:

- the carburising temperature, variation interval: 880 - 980^{o}C;
- the carburising maintenance period, variation interval: 4 - 12 hours;
- the chromizing temperature, variation interval: 950 - 1050^{o}C;
- the chromizing maintenance period, variation interval: 6 - 12 hours;
- the proportion of active elements that are chromium suppliers, variation interval: 25 - 76%.

Both thermochemical treatments were carried out in solid environments (carburising – in a mixture of charcoal and 30% $BaCO_3$ as activator; chromizing - in a mixture of chromium/ferrochromium powder, alumina and ammonium chloride in variable proportions), using refractory steel crucibles, top covered with metallic cap and clay sealed. The treatments were carried out in a silicon carbide rods heated furnace, computer assisted and programmed.

The activator proportion in the carburising mixture - $BaCO_3$, was constant for all the experiments, while the proportion of the active component that provided the chromium (the ferrochromium powder), during the chromizing, was widely varied. The cross-section microstructure and morphology of the coatings were observed using a JEOL JSM-6700F scanning electron microscope (SEM). The SEM microscope was equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer that was used to determine the chemical composition of the layers. The elemental mapping was obtained by analyzing the K lines of each element of the EDS spectra recorded in each point of the image.

The Vickers microhardness across the coating was measured on a Hanemann microhardness tester equipped with a four-sided diamond pyramidal intender. A load of 5gf and a dwelling time of 10s were applied during the tests.

The crystalline structure of the coatings was investigated by X-ray diffraction (XRD). Patterns were recorded in θ - 2θ mode using a Siemens D5000 diffractometer operating with Cu Kα radiation at 35 kV and 25 mA.

3. Results and discussion

In the Cr-C alloy system there are three stable carbides $Cr_{23}C_6$, Cr_7C_3, Cr_3C_2; a metastable carbide Cr_2C is also known [12]. Cr_2C represents an intermediate metastable phase, having a hexagonal crystallization system, which will quickly pass to its stable form, Cr_3C_2 [13]. In the presence of iron, part of the chromium atoms which from the carbides can be substituted by the iron atoms, so the chromium carbides can transform themselves into complex carbides of iron and chromium. Besides all these carbides, in the Fe-C-Cr alloy system other carbides can also occur, like $(Fe,Cr)_3C$ - cementite alloyed with chromium, or Fe_7C_3 (Ekstrom - Adcock carbide), an intermediate metastable phase, a precursor for cementite [14].

When the matrices of iron, obtained by powder metallurgy specific techniques, are subjected to carbochromizing, simple or complex carbides of chromium and iron occur, their type and their proportion being strictly correlated with the processing parameters. Thus, by reducing the proportion of the active component in the chromizing mixture, that provides chromium, but keeping the thermal and temporal parameters of the two thermochemical processes at high levels (fig. 1-4), there are no significant changes in the kinetics of the formation of carbochromized layers (45 µm – the thickness of the carbochromized layer for 76% active component providing chromium in the mixture, compared to 42 µm - the thickness of the carbochromized layer for 25% active component providing chromium in the mixture [11]).

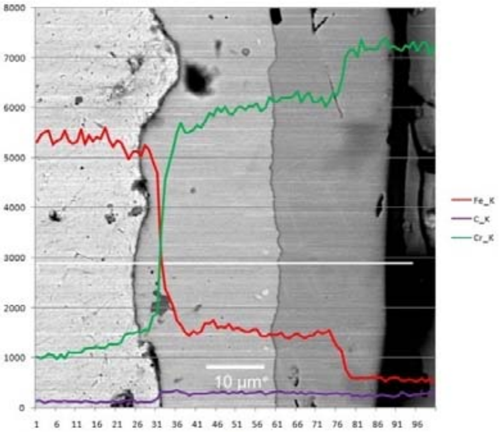

Fig. 1 SEM and EDS analysis on a sample processed in the following conditions carburized at 980°C/12 h/charcoal+30% BaCO3; chromized at 1050°C/12 h/76% active component

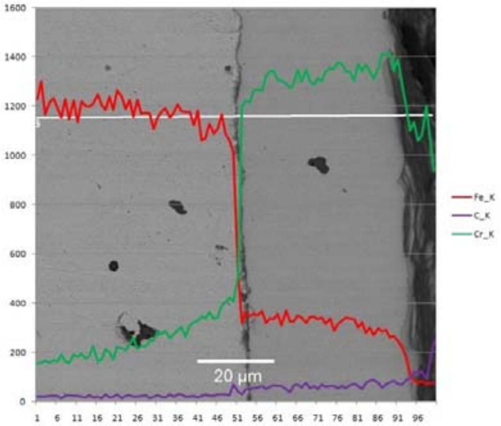

Fig. 2 SEM and EDS analysis on a sample processed in the following conditions: carburized at 980°C/12 h/charcoal+30% BaCO3; chromized at 1050°C/12 h/ 25% active component

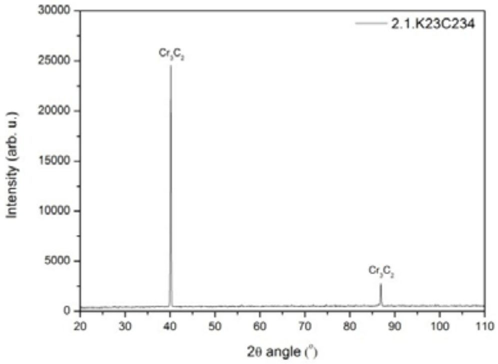

Fig. 3 XRD analysis on the sample realized in the conditions mentioned in fig. 1

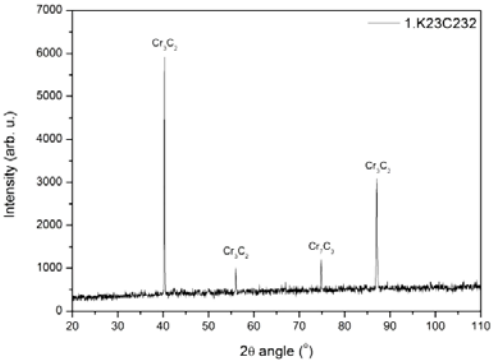

Fig. 4 XRD analysis on the sample realized in the conditions mentioned in fig. 2

Also, at the outer surface of the layer, together with the predominant carbide, Cr_3C_2, which has a low content of chromium, there is also a small proportion of a high chromium content carbide type, Cr_7C_3 (fig. 4).

The finding that environments with low chromium potential may ensure the appearance of chromium-rich carbides, compared to the environments that have higher chromium potential seems to be incomprehensible. However the x-ray diffraction analysis of sub layers areas on samples obtained in environments with a high chemical potential of chromium (fig. 5) highlight the presence of chromium-rich carbide phases. The situation seems inexplicable, but in reality it can be understood when taking into consideration the differences between the values of the coefficients of diffusion of carbon and chromium in γ-Fe and the particularities of the carbides forming process in the carbochromized layer.

Thus, $D_C^{\gamma} = 7.06.10^{-7}$ cm^2/s>>$D_{Cr}^{\gamma} = 11.2.10^{-10}$cm^2/s at 1100^{o}C for example, a phenomenon that causes a migration of carbon from the deeper areas of the layer to the surface during the chromizing process [15]. So, if the environment does not change the value of the carbon potential in time, at the surface there will be the carbon-rich carbides such Cr_3C_2 and in the surrounding sub layers areas, the chromium-rich carbides type, like Cr_7C_3.

The possibility of such a phase's sequence in the carbochromized layers obtained on iron matrices processed in crucibles not very well sealed [15], is mentioned in similar situation to that existing in our experiments.

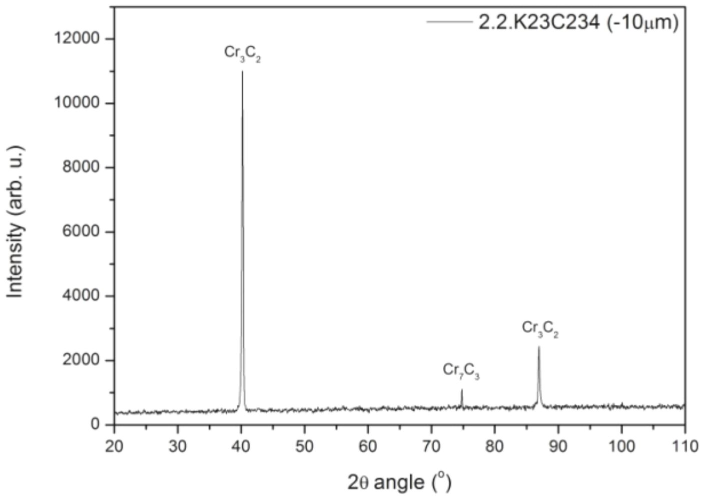

Fig. 5 XRD pattern on the sample realized in the conditioned mentioned in fig. 1, where a ~10 µm layer was removed

The occurrence of the Cr_7C_3 phase, beside the Cr_3C_2 phase, anticipates a significant decrease of the oxidation resistance for high temperatures (above 800^{o}C) [16].

By decreasing the corresponding values of the thermal and temporal parameters of carburizing (880°C, 4 hours, charcoal + 30% $BaCO_3$) and keeping constant the thermal and temporal parameters of chromizing (1050°C, 12 hours), the phase composition of the superficial layers of the carbochromized iron matrices remains apparently unchanged compared to the one mentioned before (fig. 6-9). Obviously the thickness of the resulted carbochromized layers are different (24 µm the thickness of the carbochromized layer when the environment has the lowest activity, compared to 17 µm when the environment has the highest activity [11]).

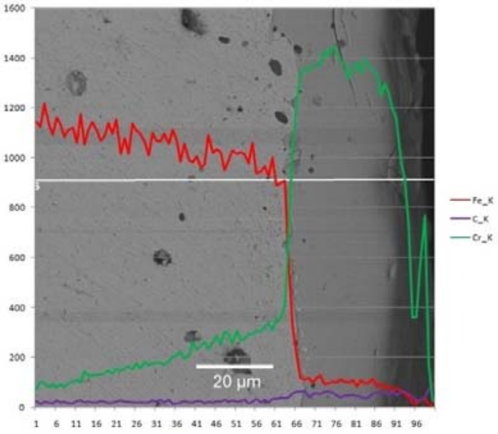

Fig. 6 SEM and EDS analysis on a sample processed in the following conditions carburized at 880°C/12 h/charcoal+30% BaCO3; chromized at 1050°C/12 h/25% active component

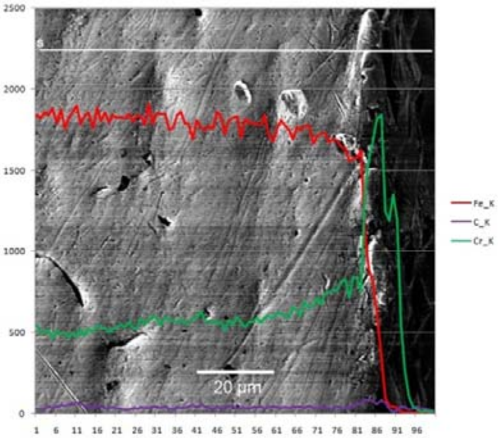

Fig. 7 SEM and EDS analysis on a sample processed in the following conditions: carburized at 880°C/12 h/charcoal+30% BaCO3; chromized at 1050°C/12 h/ 76% active component

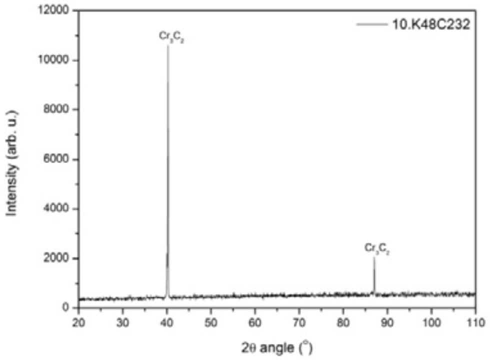

Fig. 8 XRD pattern on the sample realized in the conditions mentioned in fig. 6

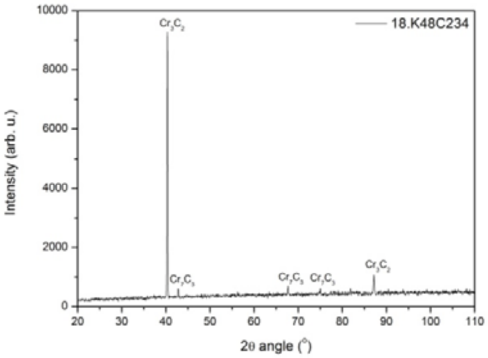

Fig. 9 XRD pattern on the sample realized in the conditions mentioned in fig. 7

In reality, the phase composition of the surface layer is reversed compared to the situation presented before; in these new processing conditions the carbides Cr_3C_2 type appear at the layer surface, when the environment chrome potential is low, and with the increase of the chrome potential, the Cr_7C_3 carbide type, also occurs.

The explication of such a situation is correlated to the value of the amount of carbon available in the layer, lower than in the previous case due to the decreasing of temperature and time during carburising; thus the conditions for the appearance of Cr_7C_3 chromium-rich carbides in chromizing environments with high chromium potential (fig. 9) are created.

During chromizing, the carbon potential of the environment is zero, therefore at the sample surface the existence or not of the carbides chromium-rich phases is related to the amount of chromium from the environment (the chromium potential of the environment) and with the amount of carbon from the layer. If the environment has high potential of chromium, the carbon from the deeper layers of the samples interacts with part of the available chromium forming chromium-rich carbides like Cr_3C_2, at 1373 K

$3Cr+2C=Cr_3C_2$; $\Delta G=-693{,}5KJ$

The excess of chromium will determine the appearance of Cr_7C_3 carbides type. When the chromium potential of the environment is reduced, the whole amount of generated Cr, by the environment for the surface will be consumed in the forming process of Cr_3C_2 carbides (fig. 8). Thermodynamically, it is very probable for the Cr_7C_3 carbide to appear, after the synthesis of Cr_3C_2 carbide due to the excess of chromium, at 1373 K

$1.5\,Cr_3C_2+2.5Cr=Cr_7C_3$; $\Delta G=-541{,}4KJ$

No matter how the experimental conditions were chosen, for the carbochromizing of the matrices of iron obtained by specific techniques of powder metallurgy in solid environment, $Cr_{23}C_6$ or the more complex $(Cr, Fe)_{23}C_6$ type of carbides were not revealed. The synthesis of these type of carbides was possible only when on the surface of the sintered and carburized (930°C, 3 hours in charcoal + 30% $BaCO_3$) iron samples has been deposited by the electrochemical method, a coating of chromium (in the following conditions: I= 600 A, T= 60°C, t= 15 hours), after that the samples were annealed at 1100°C for 6 hours in an chemically active solid environment (42% Al_2O_3 + 3% NH_4Cl + 55% mixture of chromium and ferrochromium powder with low content of carbon) (fig. 10-11).

The existence at the interface between the carburized sample surface and the electrochemically chromium deposited coating of inactive molecular combinations, results in a slower absorption and diffusion of chromium in the superficial layers, compared to the case when the chromium is in its atomic active state. According to other experimental results [17] the forming kinetics of the chromized layer, as a result of a galvanic chromium coating followed by annealing, is at least four time slower compared to gas chromizing, the differences resulting from the state in which the chromium is found, molecular (for the galvanic deposition method) or atomic (for the gas chromizing).

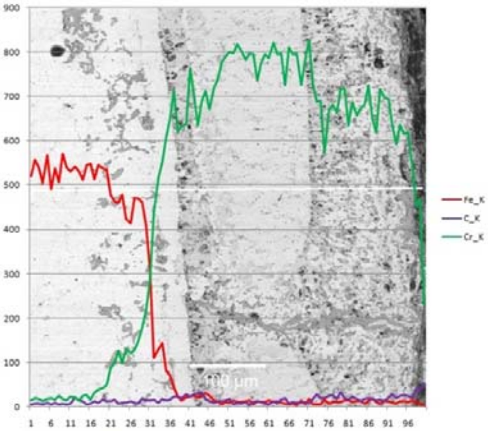

Fig. 10 SEM and EDS analysis on a sample realized in the following conditions carburized at 930°C/3 h/charcoal+30% BaCO3; electrochemically chromized: 600 A/60°C/15 hours; annealed: 1100°C/6 hours/55% active component

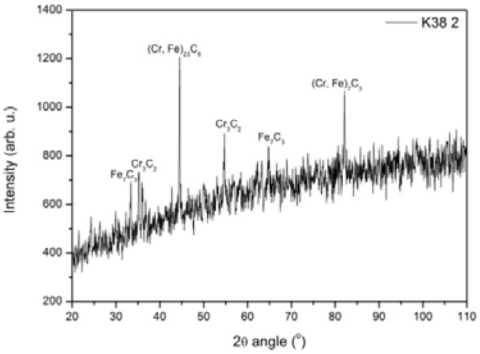

Fig. 11 XRD pattern on the sample realized in the conditions mentioned in fig. 10

In these conditions it is possible that during the annealing treatment the redistribution by diffusion of the carbon from the carburized sample and of the iron from the matrix and from the chromizing mixture (ferochromium) can occur, forming complex carbides with high and medium content of chromium, like (Cr, Fe)$_{23}$C$_6$ and (Cr, Fe)$_7$C$_3$, and metastable carbides like Fe$_7$C$_3$, even in the galvanic deposited coating. Together with all these carbides, in the electrochemically deposited coating during the annealing treatment will appear carbon-rich carbides like Cr$_3$C$_2$. The analysis of the areas in the proximity of the separation line between the galvanic deposited coating and the iron matrices by specific techniques of powder metallurgy (fig. 10) confirm that this coating is a source that provides chromium to the surface of the matrix (see the distribution of iron, carbon and chromium in fig. 10).

4. Conclusions

In the case of iron matrices, processed by specific techniques of powder metallurgy and carbochromized in solid environments, regardless the processing conditions, in the superficial layers a carbon-rich chromium carbide appears (Cr_3C_2) and together with this carbide, a small proportion of carbides with medium content of carbon can occur, in one of the following situations:

- high amount of carbon in the layer and low potential of chromium in the environment;
- low amount of carbon in the layer and a high potential of chromium in the environment.

The implications of the second carbide phase over the hardening of the surface sample are not important (the microhardness values of the two chromium carbides Cr_3C_2 and Cr_7C_3 are extremely close), but over the oxidation resistance at high temperatures is extremely important, the resistance of oxidation in hot environments decrease considerably in the presence of the Cr_7C_3 phase.

In the case of annealing samples with galvanic deposited coatings of chromium on the matrices of iron produced by specific techniques of powder metallurgy the development of chromium-rich carbides, like $Cr_{23}C_6$ can be observed.

Acknowledgments

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