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Parameters of Vacuum Process as the Factors Changing the Growth Kinetics of Chromized Layers Produced on Low-Carbon Iron Alloys by Means of CVD

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Abstract. Chemical vapour deposition of chromium on the surface of low-carbon iron alloys has been investigated using a novel CVD method that combines the low cost of pack metallisation with the advantages of vacuum technique. Chromizing processes have been carried out in a hot-wall vacuum oven with a mass spectrometer to determine the chemical composition of residual gases. The processes have been performed in chromium chlorides atmosphere at a low pressure range from 1 to 800 hPa, the treatment temperature 800 to 950°C. The effect of the vacuum level during the process and the process parameters such as time and temperature on the growth kinetics of diffusion layers has been determined. Studies of layer thickness, its morphology, its phase composition, Cr and Fe depth profiles in the diffusion zone of chromized layers have been conducted. The investigations have proved that the chromizing process under low pressure, with static vacuum instead of dynamic vacuum conditions during the holding is the most effective as far as the growth kinetics of diffusion layers is concerned. It has been shown that the kinetics of the process is controlled by the diffusion of chromium in the steel.

1. INTRODUCTION

Diffusion chromizing is one of many types of thermochemical treatment employed today for improving properties of steel surface such as microhardness, wear or oxidation, and corrosion resistance [1-7]. Corrosion resistance is characteristic of monophase layers of chromium in an α -Fe solid solution structure. Chromized layers of that structure can be obtained only on the pure iron or on special low-carbon steels stabilized by means of strong carbidizing elements (Ti, Nb, V) binding the carbon in steel as the stable carbides [8]. The diffusion chromizing by CVD consists in holding steel at the temperature over 800°C in chromium compounds (e.g. chlorides) atmosphere [9]. Chromium is transferred to the steel surface by one or more of several possible deposition reactions (of interchange, of reduction, or of thermal dissociation types) and then it diffuses in it to create a layer. The process must be conducted in the absence of air to prevent oxidation of metallic chromium which is the chromium source.

In this paper, a novel CVD method that combines the low cost of pack metallisation and the advantages of vacuum technique was investigated. The coating process was based on the formation

of chromium chlorides atmosphere in situ during the processing. A metallic chromium powder mixture with a halide activator (NH_4Cl) were used as reagents. The proposed method was obtained by means of heating a batch in a dynamic vacuum and then holding it in a static vacuum [10,11]. Usually, in vacuum techniques, the dynamic vacuum is used, maintained by continuously working vacuum pumps which take away atmosphere components from the reaction chamber. However, in such conditions, also reactive vapours e.g. chromium chlorides, necessary to produce a layer, are taken away, and consequently, the effectiveness of the process is reduced.

This problem can be avoided when we maintain the holding in a static vacuum during the chromizing process. Neither the gases nor vapours are taken away in such conditions, because a closed system is obtained when the pump is turned off. There is no information about the chromizing process carried out in such a way. The objective of this paper was to determine the effect of the vacuum level during the process and the process parameters such as time and temperature on layer diffusion growth on low-carbon iron alloys.

2.EXPERIMENTAL DETAILS

2.1 Chromizing process

The chromizing processes were carried out in a hot-wall vacuum oven with a mass spectrometer (topatron) to measure the partial pressures and to determine the chemical composition of residual gases whose range was from $M=2$ to $M=100$ of their molecular mass. The oven construction makes it possible to continuously control and to check the temperature range from 20 to 1100°C and to control the pressure from 1Pa to 10^5 Pa. Crucibles of high temperature-resistant steel were used containing steel samples in contact with a powder mixture, composed of metallic pure chromium (75%), ammonium chloride (1%) and kaolin (14%). After the crucibles were put in a vacuum retort, the pumping system started and the oven heating was activated. After the process was over, the batch was cooled in the oven.

2.2 Methods of layer examinations

The layer examinations included: phase composition, layer microstructure, thickness measurements Cr and Fe depth profiles in the layer diffusion zone. The investigations were realized on polished samples made of Armco-iron and low-carbon steel containing: 0.05% C, 0.35% Si, 0.65% Mn, 0.10% Cr, 0.09% Ni, 0.03% Nb, 0.02% Co, 0.98% Ti. The phase composition of the surface of chromized samples was determined by means of an X-ray phase analysis, employing $\text{Cu}_{K\alpha}$ and $\text{Cr}_{K\alpha}$ radiation. The layer microstructure was revealed by etching, applied at the polished cross-sections of the

specimens. An optical microscope and an X-ray microanalyser were used to determine the layer thickness. The Cr and Fe depth profiles in the layer diffusion zone were determined by means of an X-ray microanalyser too.

3. RESULTS AND DISCUSSION

3.1 Layer constitution

An X-ray surface analysis of the chromized samples made of Armco-iron and low-carbon steel revealed the presence of solid solution of Cr in α -Fe and some M_2N nitrides. The structures of chromized layers and Cr and Fe depth profiles in their diffusion zone are shown in Fig.1. The layers are unetched, as opposed to the steel core. The profiles of Cr and Fe concentration in the diffusion zone of chromized layers show that the layers should be treated as solution layers, because the sum of Cr and Fe content at successive points of concentration profiles is always about 100%. The distinct line separating the layer from the ferritic core, visible in Fig.1b, corresponded to the jump of Cr and Fe concentration on the depth profiles caused by phase transformation from γ -Fe to α -Fe at the process temperature (950°C) according to Fe-Cr phase diagram. The absence of the distinct line separating the layer from the core, visible in Fig. 1a, when the processes are carried out at lower temperatures (e.g. 800, 850°C), can be explained by the fact that diffusion below 850°C occurs mainly in ferrite without a phase transformation.

3.2 Static and dynamic vacuum influence

The scheme of temperature and pressure change during the chromizing process in dynamic and static vacuum conditions is shown in Fig. 2. The pressure increase to about 0.5 hPa over the temperature of 350°C during the heating (Fig. 2b,c) was caused by thermal dissociation reactions of ammonium chloride ($NH_4Cl \rightarrow NH_3 + HCl$) and then ammonia ($2NH_3 \rightarrow N_2 + 3H_2$). With the dynamic vacuum, when the process temperature is reached, the pressure in the oven successively decreases for nearly a value range from 0.1÷1.0 hPa to about 0.01 hPa (Fig. 2b).

In another case (Fig. 2c), when the static vacuum is used during the holding (when the vacuum pump is turned off), first the oven pressure jumps from 0.1÷1.0 hPa to 400÷800 hPa and then remains quasi-constant. An analysis of chemical composition of residual gases as soon as the process temperature is reached revealed, at the total pressure about 0.1 hPa, the presence of N_2 and CO which jointly constitute 46% of the total gas volume, H_2 about 18%, H_2O about 16% and the other residual gases such as O_2 and CO_2 below 3% (Fig. 3).

Figure 1: Microstructure and Cr and Fe depth profiles of chromized layers produced on low-carbon steel during 10h at the temperatures a - 850°C, b - 900°C.

Figure 2: Scheme of temperature changes (a) and pressure (b,c) during chromizing process:
b-dynamic vacuum, c-dynamic vacuum during the heating and static vacuum applied during the holding time.

Figure 3: Mass spectrogram of residual gasses in vacuum oven during chromizing process.

Figure 4: Layer thickness of chromized low-carbon steel as a function of temperature for a given time of treatment.

a

b

Figure 5: Layer thickness (a) of chromized low-carbon steel and square of layer thickness (b) as a function of process time for various temperatures.

A comparison was made of layer thickness produced on Armco-iron and low-carbon steel by means of static and dynamic vacuum conditions during the holding at: 850°C, 950°C within 5h and 10h; in the static vacuum conditions during the holding, the layer thickness is greater than in the dynamic vacuum, (Table 1). For instance, the layer thickness on low-carbon steel at 950°C (10h) in dynamic vacuum conditions equals 39 μ m, but in the static vacuum conditions, the layer thickness increases two times to 81 μ m.

Table1. Layer thickness on Armco-iron and low-carbon steel produced in chromizing process in dynamic vacuum and in static vacuum conditions during the holding

Steel grade	Process temperature (°C)	Process time (h)	Layer thickness (μ m)		
			Static Vacuum X_s	Dynamic Vacuum X_d	X_s/X_d
Armco-iron	850	5	27	10	2.7
		10	38	15	2.6
	950	5	53	22	2.4
		10	75	32	2.3
Low-carbon steel	850	5	32	13	2.5
		10	41	15	2.6
	950	5	59	26	2.3
		10	81	39	2.0

3.3 Influence of time and temperature on layer growth kinetics

The layer growth kinetics on low-carbon steel surface has been studied by performing a series of chromizing processes for various times: 1, 3, 5, 10 h at the temperatures of: 800, 850, 900, 950°C. The influence of time and temperature on layer thickness is illustrated in Fig. 4, which gives the variation of thickness as the function of temperature for a given time of treatment, and in Fig. 5a shows the layer thickness as the function of time at a given temperature. When the square of the layer thickness is plotted against time for various temperatures, straight lines are obtained, as shown in Fig. 5b. The linear dependence of the square of the layer thickness on the process time suggests that the chromizing process is controlled by diffusion in the steel.

4. CONCLUSIONS

The investigations carried out in this research work have proved that the vacuum level kept during the chromizing process as well as the process time and temperature influenced significantly the growth of diffusion layers. These diffusion layers produced on Armco-iron and on special low-carbon steel containing among others 0.98% Ti have a structure consisting of a solid solution

chromium in α -Fe and some M_2N nitrides. It has been shown, that the chromizing process under low pressure, in static vacuum instead of dynamic vacuum conditions during the holding, is more effective as far as the growth kinetics of diffusion layers is concerned. Moreover, it has been proved that the kinetics of the chromizing process is controlled by the diffusion of chromium in the steel.

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