The structure of the chromium plating on steel fabricated using iodine transport

S P Bogdanov¹, N A Khristiuk*¹ and M M Sychov¹²

¹Materials science department, Mechanical Engineering faculty, St. Petersburg State Institute of Technology (Technical University), Saint-Petersburg, Russia
²Institute of Silicate Chemistry of RAS, Saint-Petersburg, Russia

*nikolai.hristyuk@mail.ru

Abstract. A comprehensive study of the composition, structure, and properties of chromium-containing coatings obtained under various modes of chemical-thermal treatment (CTT) of steels with chromium has been carried out. The method of iodine transport was used as the CTT technology. On the example of Armco iron, steels 20, 45, U12 (C110W2), the effect of carbon on the phase composition and structure of coatings is shown. Based on the data obtained, the optimal conditions for obtaining coatings are recommended, providing a comprehensive increase in the operational properties of products.

1. Introduction

Improving the mechanical properties and chemical resistance of steel has been an important challenge for many decades. The economic losses from corrosion destruction of steels are estimated at billions of dollars per year [1]. One of the well-known methods for solving these problems is a surface treatment, including chemical-thermal treatment (CTT) [2] - saturation of steel with various elements at a high temperature. Diffusion chromium plating is one of the methods of chemical-thermal treatment of steels, which consists of saturating their surface layer with chromium. The versatility of chromium lies in the complex improvement of properties: corrosion resistance, wear resistance, erosion resistance, hardness, improvement of tribological characteristics [3]. The existing technology of diffusion chromium plating is characterized by simplicity of technical design and provides a complex of high corrosion-protective and wear-resistant properties and high adhesion of coatings to substrates. However, an analysis of the works of domestic and foreign authors showed that the method is energy intensive, limited by a set of agents transporting chromium [1-3]. Until now, there are disputes about the effect of the composition of steel on the structure of the resulting surface layer, and, therefore, there is no single approach to substantiate the technological modes of the diffusion chromium plating process. In the known technologies of diffusion chromium plating, the coated article is covered with a powdery mixture containing a source of chromium and an activator. The activator forms volatile chromium-containing compounds at the process temperature, which are transported to the article to be coated and, because of subsequent surface processes, the coating is formed. Currently, the most common activator is ammonium chloride NH₄Cl. The mixture for chromium plating is a source of chromium - 45-55% of chromium (or ferrochrome) powder, an activator - 0.1-1.5% of ammonium chloride, and an inert filler - 45 - 55% of aluminum oxide to prevent sintering of the charge. The process is carried out at a temperature of 950-1150°C.
The main requirement for the chemical properties of a gas transport agent is its ability to form gaseous (volatile) compounds with the transported metal, which can then easily decompose on the steel surface with the release of the parent metal. The use of iodine as an agent for gas transport reactions is known from the literature [4,5]. The advantage of iodine is its high reactivity to a number of metals, including chromium. That is especially important when metal articles of complex shape are produced for example by additive technologies [6]. However, iodine transport for the chromium plating of steels is neither used nor studied. The purpose of this work is to study the phase composition and microstructure of the surface-modified steel layers formed as a result of chromium plating by the method of iodine transport.

2. Materials and method
Experiments on diffusion chromium plating using iodine transport were carried out on samples of Armco-iron and steels 20, 45, U12 (Table 1) in the form of plates with a surface roughness of Ra = 0.10-0.15 μm. The plate and the mixture for chromium plating were loaded into a quartz reactor and heated in argon from room temperature to a predetermined process temperature, which was varied from 300°C to 1000°C with a step of 100°C. The holding time at a given temperature is from 1.5 to 6 hours. The structure was investigated by optical microscopy on a MIM-6 instrument and scanning electron microscopy using a Tescan Vega 3 instrument with an attachment for X-ray spectral microscopy (MRSA) analysis AZtec energy X-act. The phase composition was studied using X-ray diffractometer Rigaku SmartLab 3. Analysis of the elemental composition was carried out by the optical-emission method on the Spectrolab F device and by the X-ray fluorescence (RFLA) method on the Axios Advanced spectrometer. The microhardness of the coatings was investigated using a PMT-3 microhardness tester. The roughness of the coatings was determined by the contact-probe method on a Mitutoyo SJ-201P profilometer. Continuity was checked using the indicator method.

Table 1. Chemical composition of alloys.

| Alloy        | C  | Mn  | P   | S   | Cr  | Ni  | Mo  | Si  | Cu  | Al  | As  | Ti  | N   |
|--------------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Armco iron   | 0.04| 0.01| 0.005| 0.008| 0.02| 0.01| 0.005| 0.13| 0.02| <0.003| 0.001| <0.003| 0.018|
| Steel 20     | 0.18| 0.54| 0.017| 0.015| 0.02| 0.05| 0.003| 0.24| 0.04| <0.003| 0.006| <0.003| 0.009|
| Steel 45     | 0.45| 0.73| 0.016| 0.033| 0.16| 0.16| 0.02| 0.31| 0.14| 0.027| 0.012| 0.005| 0.009|
| Steel U12    | 1.25| 0.21| 0.010| 0.018| 0.11| 0.09| 0.01| 0.24| 0.15| 0.017| 0.008| <0.003| 0.007|

3. Results and discussion
It was found that with the help of iodine, the transport of chromium to the surface of all steels and Armco iron begins at a temperature of 400°C. In this case, regardless of the composition of the substrate, no continuous coating is formed (Figure 1a). The roughness of the substrates increases. So the Ra field of CTT at 400°C and a processing time of 6 hours increases 5 times and reaches 0.6 microns. It was found that the Cr content in pearlite grains is higher than in the ferritic areas of the surface. Since the carbon content in perlite differs (significantly exceeds) the content in ferrite (0.8% compared to 0.006% by weight), it can be concluded that carbon is actively involved in the coating formation process. In Armco iron, the carbon content is significantly lower than in other substrates (0.04%), but the nitrogen content is significantly higher (0.018%), therefore, the phase composition of the modified layers on Armco iron is predominantly nitride. As the carbon content in the material increases, the proportion of nitride phases decreases, gradually being replaced by carbides. An increase in the temperature of the CTO up to 500°C ensures the formation of a continuous coating. The X-ray diffraction patterns clearly show reflections from the forming phases, namely: the film on Armco-iron is CrN nitride, on all other substrates, phases of both carbides and chromium nitrides (Cr23C6 and CrN) are formed, the proportion of the latter decreases with an increase in the carbon content in the alloy. The chromium content on the surface is the highest for Armco iron and decreases...
monotonically in the series steel 20 > steel 45 > U12. Thus, in this temperature range of CTO, the formation and growth of nitrides dominate over the growth of carbides. It was revealed that the phase composition of the modified surface layer does not depend on the CTT time, and does not change throughout the entire experiment (6 h). An increase in the CTO temperature to 600°C (Figure 1b) causes a 3-fold increase in the thickness of the coatings on all alloys. The homogeneity of the phase and grain composition of the coatings is noticeably improved. The range of variation of the Cr content over the surface does not exceed 10 wt%. Starting from this temperature, the proportion of CrN decreases in comparison with the carbide phases. On medium- and high-carbon steel 45 and U12, carbon-rich Cr$_7$C$_3$ carbide begins to form, while on low-carbon steel 20 and Armco iron, only the Cr$_2$C$_6$ phase is still observed. Starting from this temperature, nitride phases are completely absent on steel U12. The effect of the carbon content in the substrate material on the thickness of the chromium-containing layer begins to manifest itself – the more carbon in the steel, the thicker the coating. This can be explained by the fact that the chemical reactions of the formation of carbides and nitrides are the driving factor of the gas transport process. The formation of continuous carbide coatings of coatings leads to a significant increase in the microhardness of the surface. The higher microhardness is expected to be observed on medium and high carbon substrates. The microhardness of steel 45 and U12 reaches up to 5 GPa, the microhardness of the surface of Armco iron and steel 20 is lower and is about 3 GPa. With an increase in the HTT temperature to 700°C, the coating on the Armco iron surface is represented by cubic CrN crystals 1–2 µm in size, inlaid in a fine-grained Cr$_{23}$C$_6$ matrix (Figure 1c).

![Figure 1](image_url)

**Figure 1.** Photo of the surface: a - steel 45, HTT mode 400 ° C, 3 hours, b - steel 20, HTT mode: 6000C, 6 hours, c – Armco iron, HTT mode: 7000C, 6 h.

The coating on U12 consists only of carbide (Cr, Fe)$_7$C$_3$. The microhardness slightly increases and is 3–5 GPa for clad armco iron, 5–6 GPa for steel 20, and 6–7 GPa for 45 and U12 steels. Insignificant surface porosity begins to develop in the obtained coatings (Figure 2a), the tendency is observed for all materials. A further increase in temperature to 800-1000°C does not cause significant changes in the morphology and phase composition of coatings on steel 20, 45, and U-12. Only their thickness increases by about 2 times. However, on Armco iron, the phase composition of the coating continues to change: the CrN phase completely disappears, instead of it, Cr$_2$N nitride, richer in chromium, appears. The surface roughness increases to Ra = 1.1 - 1.3 microns.
Figure 2. Cross sections: a - steel 20, CTE mode: 700°C, 6 hours, b – Armco iron, CTT mode: 1000°C, 6 hours, c - micrograph of the Armco iron surface, XTO 1000 °C, 6 h.

The layers formed at 900-1000°C on low- and high-carbon steels contain only one carbide phase: on steel 20 - Cr$_2$C$_6$, on steel U12 - Cr$_7$C$_3$. At that time, on medium-carbon steel 45, the coating is two-phase - the upper layer is Cr$_2$C$_6$ carbide, the lower layer is Cr$_7$C$_3$ carbide (see Figure 3). This structure is associated with the growth of the coating upon counter diffusion of carbon and chromium. All carbide layers contain a Fe impurity (2–3%) due to the diffusion of iron to the sample surface. The hardness of the samples increases to 14-16 GPa (Table 2).

Figure 3. Typical diffraction patterns of the surface of Armco iron, steel 20, steel 45, steel U12 after chromium plating at a temperature of 800-1000°C.

When Armco-iron is clad in the temperature range 900-1000°C, a multilayer structure is formed. Only the Cr$_2$N phase is present on the surface, and a layer of Cr$_2$C$_6$ carbide is formed under it. The thickness of the nitride layer is very small (at 1000°C, 6 hours), therefore, chromium nitride is absent
in the diffractogram. The formation of Cr$_{23}$C$_6$ carbide in coatings on Armco iron occurs after the binding of nitrogen dissolved in iron and is caused by the presence of carbon in the initial sample (0.04%) (Table 1). A diffusion zone of a solution of chromium in iron forms behind it, in which the Cr content gradually decreases from 30% to 15% deep into the substrate. The boundary of this zone is sharply limited by the drop in the chromium content practically to the level of impurities in the base metal (Figure 4).

![Figure 4](image)

**Figure 4.** Map of Cr distribution in a cross-section of clad Armco-iron, HTT mode 900 °C, 6 h. 1 - Cr$_2$N, 2 - Cr$_{23}$C$_6$, 3 - γ-phase, 4 - α-phase.

This phenomenon is due to the diffusion of chromium into austenite and dissolution in it. At the same time, according to the Fe – Cr diagram [6], in the temperature range 800-1400°C, a phase transition occurs - the transformation of austenite (γ-phase) into ferrite (α-phase). The transformation at 900-1000°C occurs with an increase in the chromium content in the alloy over 13% by weight. Indeed, it was found that the minimum concentration of Cr in this layer is 15 wt%. Thus, this boundary is the region of transition from the γ-phase to the α-phase.

The study of transverse sections of coatings on steels shows the absence of a developed diffusion zone; the distribution of Cr and Fe in the coating is discontinuous, in contrast to Armco-iron. At the same time, the thickness of the coatings is always lower than in the case of Armco-iron and is directly proportional to the carbon content in the material to be coated. These regularities are explained by the fact that the formation of Cr$_{23}$C$_6$ and Cr$_7$C$_3$ carbides hinders the diffusion of Cr and C towards each other, therefore, the coating grows more slowly than on Armco-iron. Thus, the growth rate determines the carbon content of the material. The resulting coatings are characterized by longitudinal uniformity and continuity. The microhardness of the surface is 5 GPa (Table 2).

| Material     | Microhardness, GPa |
|--------------|--------------------|
| Armco iron   | 5                  |
| Steel 20     | 14                 |
| Steel 45     | 14                 |
| Steel U12    | 16                 |

The roughness of the surface increases to 1.0 microns. Steels have surface porosity. This structure is effective under lubricated friction conditions. Porosity is inherent in the carbide phase, and it is in
these areas of the surface that all materials exhibit an increased Fe content. The iron content in the surface layer is higher for alloys with high carbon content and reaches 13% for U12 steel. The observed phenomenon is explained by the fact that Fe is etched from the substrate and carried away by iodine. The effect was confirmed by measurements of the weight of the samples during CTO. At temperatures up to 700-800°C, despite the formation of a continuous coating with a thickness of up to 3 microns, the weight of the samples decreases by 20-30 g/m². The weight gain of blanks begins only after 900°C and amounts to 10-20 g / h.m². In the case of Armco-iron cladding, the zero balance point is 700°C.

4. Conclusions
A comprehensive study of the composition, structure, and properties of chromium-containing coatings obtained under various modes of the CTO process has been carried out. The change in the phase composition of the coatings is shown depending on the substrate material. It has been established that the main driving force of the gas transport process at all temperatures is the formation of chemical compounds of chromium: carbides and nitrides. It was found that the chemical composition of the coatings mainly depends on the temperature of the CTO and the carbon content in the steel, while a change in the processing time at a constant temperature practically does not lead to a change in this parameter. Based on the data obtained, it is possible to recommend the optimal conditions for obtaining coatings that provide a comprehensive increase in the operational properties of products. Temperature - 900°C, time from 2 to 6 hours, depending on the purpose of the coating.

Acknowledgments
The study was supported by a grant from the Russian Science Foundation (project 21-73-30019).

References
[1] Czerwinski F 2012 Heat Treatment – Conventional and Novel Applications (Published by InTech, Janeza, Croatia) p. 408
[2] Loskutov V F and others 1991 Diffusion carbide coatings (Kiev: Technika) p.168
[3] Wang Q J and Chung Y W 2013 Encyclopedia of tribology (Springer science + Business Media: New York) p. 4192
[4] Rolsten R F 1968 Iodide metals and metal iodides (M.: Metallurgy) p. 524
[5] Bogdanov S P 2011 Obtaining coatings on powders by the method of iodine transport Glass Physics and Chemistry 37(2) 229-37
[6] Khvan A V, Hallstedt B, Christoph B 2014 Broeckmann thermodynamic evaluation of the Fe–Cr–C system CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 46 24 – 33