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Chromium plating of steel parts using the thermoemission field

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ABSTRACT

Experimentally, it was found that if a second metal component is added to the technological backfill during thermal diffusion chromium plating or if the inert separating additive of corundum is replaced by minerals-solid electrolytes, a current appears in the technological backfill directed to the saturable part. The appearance of an electric field is due to the emission of electrons (metal components of the filling) and oxygen anions (solid oxide electrolytes). It is determined that the emission flux makes a contribution to the saturation process that is commensurate with the diffusion flux formed according to Fick's laws. Experiments show an acceleration of diffusion processes and an increase in the depth of the diffusion layer of chromium by 2–2.5 times.

KEYWORDS

thermal diffusion chromium plating • thermal emission field • diffusion depth

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Introduction

To protect the surface of parts of pipeline structures from external factors, to give them corrosion resistance, high hardness and wear resistance, the technology of thermal diffusion chromium plating has been used for many years [1–7]. This technology consists in heating parts in a sealed container with filling from a mixture of powders: chromium (ferrochromium), corundum and activators NH_4Cl , NH_4I at a temperature of 900–1000 °C. In the process of holding at the heating temperature, the formation of chromium halides occurs, their deposition on the surface of the part, decomposition and subsequent diffusion of atomic chromium into the metal of the part with the formation of a diffusion layer. The layer depth depends on the temperature, the duration of the process, and the carbon content in the steel [2,8–16].

Attempts to improve the traditional technology of thermal diffusion chromium plating consisted mainly in carrying out two or more component saturation with boron, vanadium and manganese, molybdenum [1,17–23]. In our work on joint chromium plating with tungsten and nickel, it was found that, in addition to increasing hardness, the introduction of the second component increases the depth of chromium diffusion on the metal surface. Thus, during thermal diffusion chromium plating of steel 35Kh2N3 at a temperature of 1000 °C for 24 hours without additional addition to the technological mixture, the depth of the diffusion layer was 30 μm [24], with joint saturation with nickel under the same conditions – 40 μm [25], with the introduction tungsten powder, the chromium diffusion depth was 55 μm [26]. From the point of view of only the concentration theory of diffusion, described by Fick's laws, it is impossible to explain the increase in the diffusion layer by 1.52 times at constant temperature-time parameters of

the process. At the same time, tungsten is known as an emissive electronics material used to make cathodes. The emission of electrons by tungsten occurs regardless of whether the tungsten sample is heated by passing current or by heat flows from another source. It has been suggested that the acceleration of chromium diffusion may be due to the electron flux emitted by the tungsten particles. Since iron and steel are always positive electrodes [27], it is obvious that, firstly, the resulting emission flux of negatively charged particles must be directed to the saturating part, and secondly, this flux must lead to the appearance of an electric current in the saturating mixture.

In developing the idea of the appearance of an emission current in a saturating mixture, it became necessary to determine the possibility of using not only metal components as emitter additives, but also oxides, which can play two roles - to be a separator for metal particles of the saturating element powder and to create an additional thermionic flow that promotes acceleration diffusion. It is known, for example, that solid electrolytes of the $ZrO_2 + 10\% Y_2O_3$ type are most widely used in metallurgy. A distinctive feature of these substances is 100 % anionic conductivity O^{2-} . Taking into account this feature of solid electrolytes, the possibility of using oxide additives in chemical-thermal treatment is considered for the first time.

The purpose of this work is to determine the electrical characteristics of metal- and oxide-containing saturating mixtures and to establish their relationship with the depth of the emerging diffusion layer.

Methods

To measure the current arising in the technological backfill, an installation was designed (Fig. 1). The main element of the installation is a cell - a cylindrical corundum crucible with a diameter of 30 mm and a height of 80 mm. Two iron wire electrodes 1.4 mm in diameter were placed in the crucible. A sample of 35Kh2N3 steel $25 \times 10 \times 8$ mm in size was welded to one electrode. The distance between the electrodes in the cell was maintained at 18 mm in all experiments. The technological mixture filled the volume with the cell by 80 % and was covered with asbestos cardboard. Further, a mixture of silicocalcium was covered with a layer of 6-8 mm, then, after a layer of asbestos, graphite powder, which was again covered with asbestos. To exclude a short circuit in the layer of corundum with graphite, the electrodes were insulated with corundum tubes. The electric circuit current was measured in cells with metal and oxide emitters added to saturating mixtures. The compositions of the investigated technological fillings are given in Table 1.

The electrical measuring cells were placed on a pallet, 2 pieces each, and placed in a Nabertherm 41/H chamber furnace. To measure the current that occurs during heating in the circuit | electrode 1 → saturating mixture → electrode 2 |, the electrode leads were connected to an APPA-207 digital multimeter. The furnace was heated up to 1050 °C. The furnace heating program was set in such a way that heating to 500 °C was carried out continuously, then every 50 °C a 10-minute exposure was made to measure the current in the circuit. The temperature in the furnace was controlled using a platinum exemplary thermocouple.

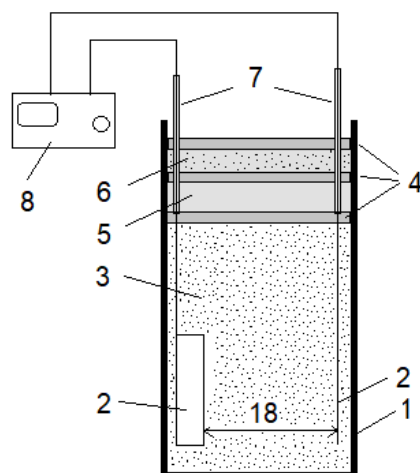


Fig. 1. Scheme of the measuring cell for studying the electric field formed during chemical-thermal treatment: 1 – cell body; 2 - electrodes; 3 - technological backfill; 4 - asbestos sheet; 5 – silicocalcium powder; 6 – graphite powder; 7 - insulating corundum tubes; 8 - digital multimeter

Table 1. Compositions of saturating mixtures

No. of the mixture	Main saturating component	Additive to the saturating mixture		Corundum, (powder, fraction 140 μm), wt. %	NH_4Cl , (powder, fraction 0.5–2.0 mm), wt. %
	Chromium, (powder, fraction 150 μm), wt. %	Type of additive	Mass. %		
1	50	-	-	50	4
2	40	W (150 μm)	10	50	4
3	40	Ni (150 μm)	10	50	4
4	45	CaWO_4	15	40	4
5	45	MgO	15	40	4
6	45	$\text{MgO}+2\text{CaO}\cdot\text{SiO}_2$	5+10	40	4
7	45	$\text{WO}_3+2\text{CaO}\cdot\text{SiO}_2$	5+10	40	4
8	45	$2\text{CaO}\cdot\text{SiO}_2$	15	40	4
9	45	Y_2O_3	15	40	4

After complete cooling, the samples were removed from the saturating mixture, a fragment 10x8x8 mm in size was cut off from each sample to make transverse microsections. Then, the transverse sections of the samples were examined using a Jeol JSM 6460LV electron microscope equipped with an Oxford Instruments X-ray microanalysis (XMS) attachment. By point MRS analysis in the direction from the surface to the center of the section of the part, the composition of the diffusion layer was studied, and the depth of chromium diffusion was determined.

Results and Discussion

The results of measuring the magnitude of the thermionic current that occurs in the filling with two iron electrodes at 1000 °C between the cells with the addition of metal and oxide electron emitters in technological fillings are shown in Fig. 2. It can be seen that without the supply of additional electricity from the outside, electric fields appear in the cell, due to the composition of the technological mixture and temperature.

The magnitude of the emerging thermionic field for both metal and oxide additives varies greatly (Fig. 2). In contrast to all other systems under study, CaWO_4 emission begins at 500 °C and grows dynamically, reaching a maximum of 0.65 mA at 850 °C. For metal additives (W, Ni) and most oxide additives, a noticeable emission of charged particles begins at temperatures up to 800 °C. The strength of the resulting current when using metal additives is 0.14 and 0.21 mA, respectively, for Ni and W. $\text{MgO} + 2\text{CaO SiO}_2$ and 2CaO SiO_2 can be isolated from oxide additives, providing a thermionic current of 0.05 and 0.30 mA, respectively. In mixtures with other oxide additives, the current strength does not exceed 0.003 mA.

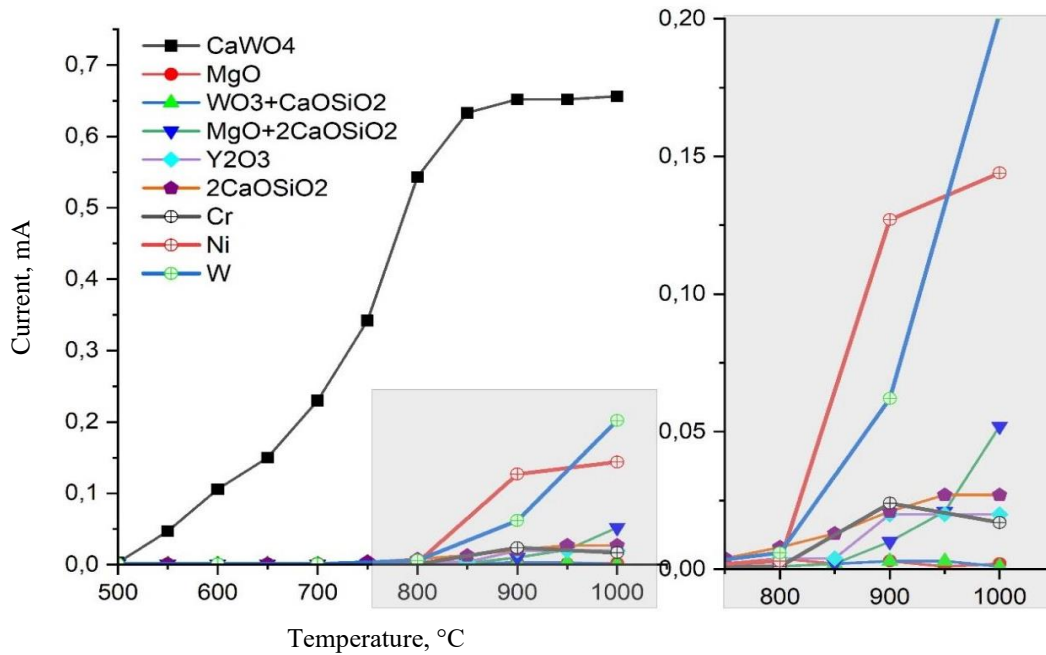


Fig. 2. Values of current strength in backfills

To establish the relationship between the magnitude of the emerging thermionic current and the depth of chromium diffusion, transverse sections of the electrode sample were studied.

The results of measuring the diffusion depth of chromium after 1 hour of exposure at 1000 °C from the strength of the emission current arising in the backfill are shown in Fig. 3. According to the data obtained, with an increase in the values of the emission current arising in the backfill, the depth of chromium diffusion also increases.

In the process of diffusion saturation of parts, refractory metals are a source of electrons. Oxides and their compounds are a source of oxygen anions. The mixed flow of electrons and oxygen anions is the field involved in the saturation of the surface of the parts with metal, which in atomic form moves to the surface of the workpieces. On the surface of the parts, the atoms of the diffusing substance move to the surface layer, which is described by Fick's 1st law [28,29]:

$$J_k = -D \frac{dc}{dx} = \frac{\Delta G_k}{S \cdot \Delta \tau}, \quad (1)$$

where J_k is the amount of diffusing substance k that passes per unit of time through a section of a unit area located at a right angle to the direction of the diffusion flow, $\frac{\text{kg}}{\text{m}^2 \cdot \text{sec}}$;

$\frac{dc}{dx}$ is the concentration gradient k ; D is the diffusion coefficient (m^2/sec); ΔG_k is an amount of substance, kg; $\Delta\tau$ is time, sec; S is square, m^2 .

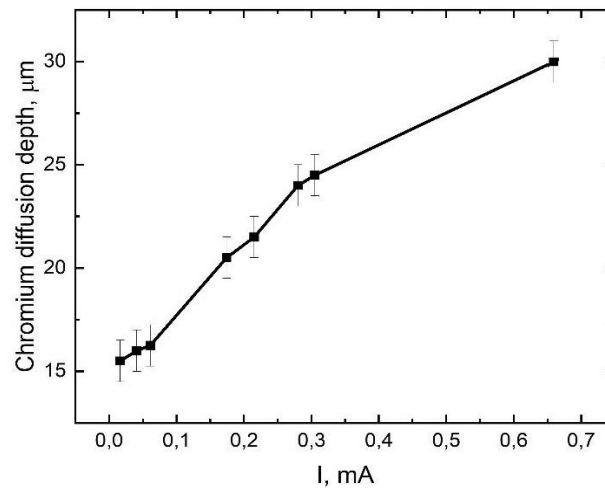


Fig. 3. Dependence of the chromium diffusion depth on the thermionic current

Since the minus sign in Fick's first law only indicates the direction of mass transfer, the amount of the transferred substance can be determined:

$$\Delta G_k = \left| -D \frac{dc}{dx} \right| \cdot S \cdot \Delta\tau. \quad (2)$$

The calculation of the diffusion coefficient D is presented in [30] and can be automated. Thus, all factors of Eq. (1) are definable and the amount of substance transferred by the concentration field is calculable.

It is more difficult to determine the participation of the emission field of oxygen anions created by the ceramic material of the technological mixture, and its share in the transfer of metal in the process of chemical-thermal treatment. As shown above, the strength of the resulting current is determined by the composition of the ceramic part of the backfill at a constant weight ratio (55–60 wt. % ceramics; 45–40 wt. % chromium). An analysis of the experimental results (Fig. 1) allows us to conclude that a solid powder mixture of metal and ceramic phases deposits a chromium layer on the sample surface in proportion to the passed electricity. What can be considered an application of Faraday's law for powdered electrolytes:

$$G_k = z \cdot Q, \quad (3)$$

where G_k is a mass of settled substance k , released on the electrode, kg; z is an electrochemical equivalent, $kg/(A \cdot h)$; Q is an amount of electricity passed ($Q = I \tau$); I is a direct current passing through the phase boundary, A; τ is the duration of the passage of current, hour. That is, from Eq. (3):

$$G_k = z \cdot I \cdot \tau. \quad (4)$$

The electrochemical equivalent z is the amount of substance that reacted as a result of the flow of a unit amount of electricity. The equation for calculating the electrochemical equivalent is as follows:

$$z = \frac{M}{n \cdot F}, \quad (5)$$

where M is the molar mass of the reagent; n is the valency of the diffusing substance; F is the Faraday number or constant, $F = 96486 \approx 96500$ C/mol.

Using Eqs. (4) and (5) it is possible to determine the final equation for Faraday's law in powder electrolytes:

$$G_k = \frac{M}{n \cdot F} \cdot I \cdot \tau \quad (6)$$

Thus, taking into account the fact that in one technological process the diffusing element is transferred to the surface of samples (parts) in different fields, using Eqs. (2) and (6) we can write the general equation for the transfer of matter in the process of diffusion metallization:

$$\sum G_k = \left| -D \frac{dc}{dx} \cdot S \cdot \Delta\tau \right| + \frac{M}{n \cdot F} \cdot Q \cdot I \cdot \tau. \quad (7)$$

The resulting equation corresponds to the postulates of K. Wagner about the independence of the transfer of particles from the conditions [29] from the concentration and electric emission fields.

Conclusions

1. The formation of emission fields due to the release of electrons from metals and oxygen anions from amorphous solid electrolytes in technological fillings during thermal diffusion chromium plating has been proved;
2. A quantitative assessment of the participation of electric emission fields and concentration fields in saturation processes was carried out;
3. The possibility of accelerating the process of chromium diffusion during thermal diffusion saturation of steel parts by introducing additives-emitters of electrons or O^{2-} anions into the saturating mixture has been proved;
4. It has been determined that the most promising and cost-effective emitter additives are oxide additives $2CaO \cdot SiO_2$, $CaWO_4$, which can partially or completely replace inert refractories in the filling.

References

1. Samuel RL, Lockington NA. *Metal Treatment and Drop Forging*. 1951.
2. Lyakhovich LS. *Chemical-thermal treatment of metals and alloys*. Moscow: Metallurgy; 1981. (In Russian)
3. Kitaev NI, Yakimovich YuV, Shigaev My, Pichkhidze SYa. Thermal diffusion chromium plating of structural carbon steel 20 by high frequency currents. *Voprosy Materialovedeniya*. 2021;106(2): 137–145. (In Russian)
4. Goyushov RG. Physical and mechanical properties of marine engine parts restored by diffusion chrome plating. *Universum*. 2023;10(115): 41–44.
5. Boblyov EE, Storozhenko ID. Diffusion metallization of carbide cutting tools as a way to improve the surface treatment quality. *Journal of Physics: Conference Series*. 2019;1399(4): 044084.
6. Castle AR, Gabe DR. Chromium diffusion coatings. *International Materials Reviews*. 1999;44(2): 37–58.
7. Schwarz S, Rosiwa SM, Musayev Y, Singer RF. High temperature diffusion chromizing as a successful method for CVD-diamond coating of steel—Part II. *Diamond and Related Materials*. 2003;12(3–7): 701–706.
8. Zancheva L, Hillert M, Lange N, Seetharaman S, Staffansson LI. On the formation of carbide coatings by chromizing carbon steels. *Metall. Trans. A*. 1978;9: 909.
9. Bogdanov SP, Khristiuk NA, Sychov MM. The structure of the chromium plating on steel fabricated using iodine transport. *Journal of Physics: Conference Series*. 2021;1967: 012039.
10. Zhang S, Zhang H, Zhang H, Zhao X, Li Y. Study on Diffusion Kinetics and Law of Chromium on the Surface of Low-Carbon Steel. *Coatings*. 2023;13(1): 98.

11. Zieliński M, Koniorczyk P, Surma Z. Studies on Influence of Chromium Layer on Inner Surface of Steel Tube on Heat Transfer. *Appl. Sci.* 2023;13: 5523.
12. Zhang SX, Li YG, Wang C, Zhao XP. Preparation of a Cr coating on low-carbon steel by electrodeposition in a NaCl-KClNaF-Cr₂O₃ molten salt. *Int. J. Electrochem. Sci.* 2019;14(1): 91–101.
13. Veselovsky A, Troyanovskaya I, Erofeev V. Predicting the Thickness of the Hardening Coating during Diffusion Metallization of Cast Iron. *Materials Research Proceedings.* 2022;21: 51–55.
14. Pastukhov A, Sharaya O, Timashov E, Bakharev D. Method of justification of machine parts hardening modes. *Engineering for Rural Development.* 2021;20: 74–79.
15. Wang B, Qiu F, Barber GC, Pan Y, Cui W, Wang R. Microstructure, wear behavior and surface hardening of austempered ductile iron. *Journal of Materials, Research and Technology.* 2020;9(5): 9838–9855
16. Veselovsky AA, Dema RR, Kalugina OB, Nefedyev SP. Determination of parts tolerances in friction knots of grey and nodular cast iron with thermal diffusion platings vanadium and chrom. *MATEC Web of Conferences.* 2017;129: 02043.
17. Lim SC, Lim CYH, Lee KS. The effects of machining conditions on the flank wear of TiN-coated high speed steel tool inserts. *Wear.* 1995;181/183(2): 901–912.
18. Sen S, Sen U, Bindal C. An approach to kinetic study of borided steels. *Surface & Coating Technology.* 2005;191(2-3): 274–285.
19. Aghaie-Khafri M, Mohamadpour Nazar Abady M. A Study of Chromo-Boronizing on DIN 1.2714 Steel by Duplex Surface Treatment. *JOM.* 2012;64(6): 694–701.
20. Meier GH, Cheng C. Diffusion chromizing of ferrous alloys. *Surface and Coating Technology.* 1989;39/40: 53-64.
21. Ennis PJ, Quadackers WJ. High chromium martensitic steels-microstructure, properties and potential for further development. *VGB PowerTech.* 2001;81: 87–90.
22. Quadackers WJ, Piron-Abellan J, Shemet V, Singheiser L. Metallic interconnectors for solid oxide fuel cells – a review. *Mater. High Temp.* 2003;20(2): 115–127.
23. Singheiser L, Huczowski P, Markus T, Quadackers WJ. In: Richardson JA. (ed.) *Shreir's Corrosion.* Oxford: Elsevier; 2010.
24. Shaburova YUD, Shaburova NA, Pashkeev IYu. Investigation of the distribution of chromium in the diffusion layer during chromium plating of steel 35Kh2N3. *Bulletin of SUSU. Series Metallurgy.* 2022;22(1): 24–32. (In Russian)
25. Shaburova NA, Pashkeev IYu. Influence of the conditions of joint saturation of steel with chromium and nickel on the depth of the diffusion layer. *Ferrous metallurgy. Bulletin of Scientific, Technical and Economic Information.* 2022;78(6): 542–548.
26. Shaburova NA, Pashkeev IYu. Distribution of chromium and tungsten in the diffusion layer of steel 35Kh2N3 at joint thermal diffusion saturation. *Bulletin of SUSU. Series Metallurgy.* 2022;2: 41–52. (In Russian)
27. Rogelberg IL, Beilin VM. *Alloys for thermocouples.* Moscow: Metallurgy; 1983. (In Russian)
28. Darken LS, Gurri RV. *Physical chemistry of metals.* New York: McGraw-Hill; 1953.
29. Chebotin VN. *Physical chemistry of a solid state.* Moscow: Chemistry; 1982. (In Russian)
30. Umansky YaS, Finkelstein BN, Blanter M. *Physical basis of metallurgy.* Moscow: Metallurgizdat; 1955. (In Russian)

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