Chromizing of Iron

Difuzijsko kromanje železa

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In the paper, the theoretical aspects of CVD processes of iron chromizing and the comparison with the PVD process, developed by the authors for professional electronic industry are presented.

V sestavku so podani teoretični vidiki CVD postopkov difuzijskega kromanja železa in primerjava s PVD postopkom, ki so ga ovtorji razvili za potrebe profesionalne elektronike.

1 Introduction

Corrosion is one of the most frequent and the most undesired processes on the surface of metals and alloys. Since corrosion is a surface reaction, all types of protective coating must be involved to change the behaviour of metallic component in the surface composition. This change can be achieved by addition of a different material or in the form of outer skin, which provides a barrier between the body and the surrounding corrosive medium. The form of coating is the most common; it includes paints, plastics, metals deposited by electroplating etc. It is also possible to modify the chemical composition of the surface to be protected, by diffusion of a suitable metal or an element into it which will combine with the parent metal or alloy and provide the required resistance to the corrosive medium. Such formed surface alloys are called diffusion coatings. The dimensional change of the protected specimen is smaller than the thickness of the effective surface alloy and it may be neglected.

Chromium diffusion—chromizing is probably one of the most versatile types of diffusion coatings and it is applied to achieve resistance to corrosion, thermal oxidation and abrasion for iron, steel, stainless steel, nickel and its alloys, molybdenum, tungsten and its alloy, etc.

2 Technological development of chromizing

The first attempts to achieve a chromium rich surface on iron by the diffusion process were made by Kelly in 1923[2]. Iron specimens were buried into chromium powder and treated in reducing atmosphere. A chromium rich layer, about 125 μm thick, formed after 4 hours heating at 1300°C, was a protecting layer with good adherence to the underlying metal, resistant to corrosion, as well as to thermal oxidation and, therefore, very interesting for wide commercial use.

Similar investigation was made by H.S. Cooper in 1938[2]. The process of chromizing was applied in a reducing atmosphere at the temperature of 1300°C, lasting 24 hours; the thickness of chromized layer was 250 μm.

A high processing temperature was disadvantage of both procedures.

The chromizing process has undergone considerable development changes over the years and it has been the subject of careful and detailed studies. A major achivement was

the introduction of volatile halides. L.H. Marshall developed the first CVD (chemical vapour deposition) procedure of chromizing, using the volatile halides at the processing temperature of 1050°C.

Modern chromizing processes like DAL, BDS, etc. are based on the above mentioned principle[3,4].

Simultaneously, the first experiments of vacuum diffusion chromizing were performed by Hicks as early as 1932. Particles of pure iron were buried in a chromium powder and heated for 96 hours at 1200°C in a vacuum of $4 \cdot 10^{-2}$ mbar. Eight years later, Cornelius and Bollenrath[8] obtained similar results in their experiments; chromium concentration profiles were determined by the X-ray analysis. Further, this process was described by Gorbunov and Dubinin[12].

In Slovenia the vacuum chromizing process (PVD—physical vapour deposition) has been developed at the Institute for Electronics and Vacuum techniques together with the Institute of Metals and Technologies[4,5,17] and has been used for diffusion chromium coating of iron parts of magnetic circuit for miniature relays.

3 Fe-Cr constitution diagram

The iron-chromium constitution diagram is shown in **Figure 1.** At approximatelly 1000°C, it can be seen that the austenite microstructure of the iron remains unchanged until a concentration of approximately 12% chromium is reached when chromium is deposited and it diffuses inwards. At higher chromium concentrations, the microstructure becomes ferritic; continuation of chromizing causes moving of the alpha/gamma boundary into interior. During cooling the ferrite surface layer remains unchanged, while inner austenite is transformed into ferrite. This recrystallization of inner region with less than 12% Cr causes that boundary with 12% Cr is good visible, **Figure 2.** The depth to which extends the 12% Cr boundary is taken as the thickness of chromized layer, **Figure 3.**

Since the rate of diffusion of chromium is greater in ferrite than in austenite, there is a rapid rise in the chromium concentration of the coating towards the surface, and beyond the 12% Cr boundary there is a sharp concentration drop at the ferrite/austenite boundary. Grain boundary diffusion occurs too, but it has a little effect on the coat thickness, **Figure 4.**
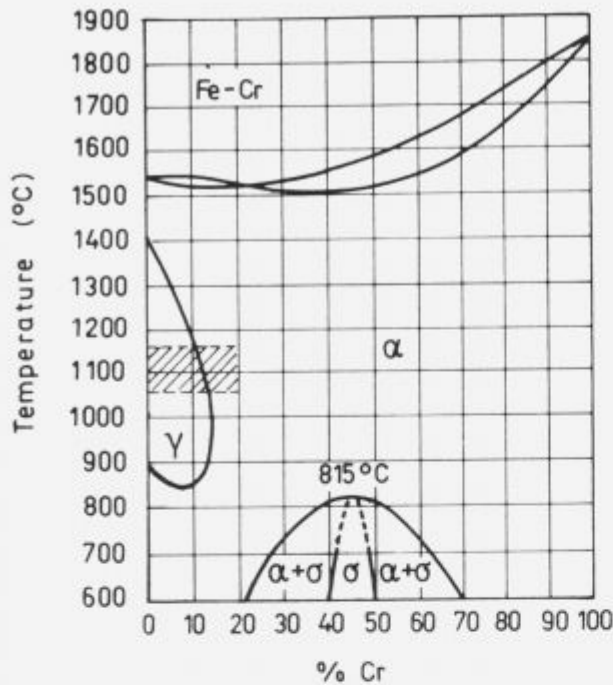
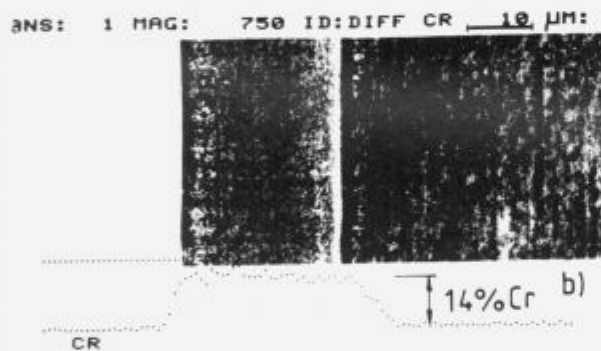Figure 1. Iron—Chromium diagram[5].
Slika 1. Fazni diagram Fe—C[5].

Figure 2. a) Micro-section of vacuum chromized sample. A sharp α/phase boundary is visible (nital etched). b) Cr concentration profile of the same sample.
Slika 2. a) Metalografski posnetek vakuumsko kromanega vzorca železa; vidna je ostra fazna meja alfa/gama (jedkano z nitalom). b) Koncentracijski profil kroma posnet z elektronskim mikroanalizatorjem na istem vzorcu.

The alloyed layer is generally called a coating, but it must be clearly distinguished from the coatings produced by electroplating and spraying processes, since there is no diffusion. The chromized coating represents an inseparable part of the treated specimen, the composition is changing from the surface to the core.

4 Mechanism and kinetics of cromizing the iron

4.1 Chromizing technique with volatile halides

In these processes chromium is brought to the surface of the iron heated to 900–1150°C as a gaseous compound, e.g. chromium chloride, where it is deposited in atomic form by a chemical reaction.
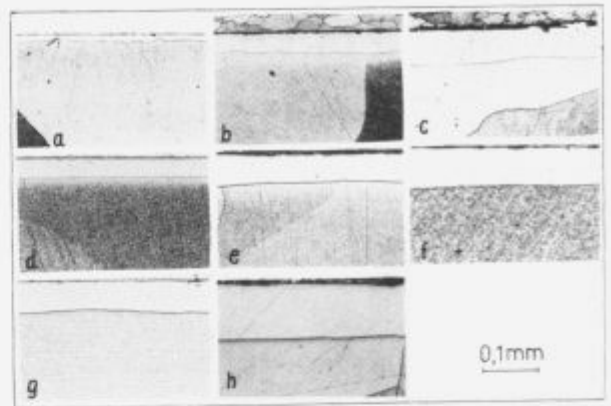

Figure 3. Microsections of vacuum chromized iron samples at: 1050°C (a) 3 hours, (b) 8 hours (c) 12 hours, 1100°C (d) 3 hours, (e) 8 hours, (f) 12 hours, 1150°C (g) 3 hours, (h) 8 hours. Nital etched.
Slika 3. Metalografski posnetki vakuumsko kromanih vzorcev železa pri: 1050°C (a) 3 ure, (b) 8 ur (c) 12 ur, 1100°C (d) 3 ure, (e) 8 ur, (f) 12 ur, 1150°C (g) 3 ure, (h) 8 ur. Jedkano z nitalom.
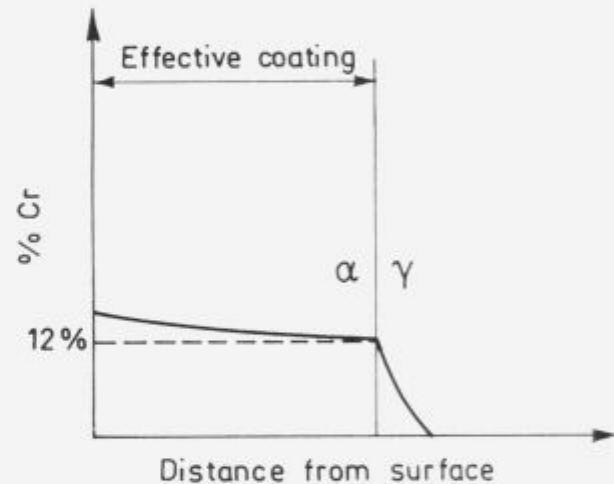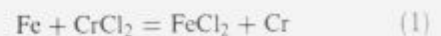

Figure 4. Chromium concentration profile in α-FeCr layer.
Slika 4. Gradient kroma v kromani plasti.

In many chromizing techniques, chromium chloride is applied and an atmosphere containing hydrogen is maintained in the reaction chamber.

The deposition of chromium on iron is described with the following equations:

- Interchange

$$Fe + CrCl_2 = FeCl_2 + Cr \qquad (1)$$

- Reduction

$$CrCl_2 + H_2 = 2HCl + Cr \qquad (2)$$

- Dissociation

$$CrCl_2 = Cl_2 + Cr \qquad (3)$$
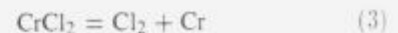
In the reaction (1) an atom of iron is removed from the surface for each deposited chromium atom. Since iron and chromium atoms are similar in weight and size, there occur

only slight mass and dimensions changes of iron specimens after the treatment. The reaction is reversible and the equilibrium chromium concentration at the surface depends on the relative vapour pressures of iron and chromium chlorides in gaseous phase.

Reactions (2) and (3) are catalysed by the iron surface. Theoretically the surface chromium concentration may approach 100 per cent, but since it is assumed that the catalytic activity of the iron surface drops with the increasing chromium content, the concentration of chromium is limited. The mass and dimension change are equivalent to the amount of deposited chromium.

Generally, the volatile halides are used for transport of chromium atoms to the surface of iron, where they are adsorbed and diffuse inwards.

In **Figure 5** the layout of BDS (Becker, Daeves, Steinberg) process, a typical CVD process, is shown.
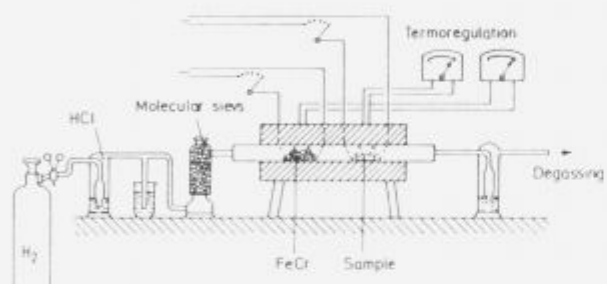

Figure 5. The layout of BDS (Becker, Daeves, Steinberg) process, typical CVD process, is shown.
Slika 5. Shematičen prikaz CVD-BDS postopka.

Vacuum chromizing

There are two possible processes of supplying an iron surface with the chromium atoms:

- transfer due to the close contact of iron surface and chromium granulate enabling the surface diffusion of Cr
- absorption of Cr vapour through the formed gaseous phase

In vacuum chromizing the growth of $\alpha - FeCr$ layer is controlled by two processes:

1. *The arrival and condensation of Cr atoms on the surface of the specimen* given by the condensation rate w:

$$w = \frac{1}{2\pi}\sigma_k p_{Cr}\sqrt{\frac{M}{RT}} \qquad (4)$$

$$w = 0.044\sigma_k p_{Cr}\cdot\sqrt{\frac{M}{T}} \qquad /\text{g cm}^{-2}\text{s}^{-1}/ (5)$$

where σ_k is the condensation coefficient; p_{Cr} (mbar) is vapour pressure; M is Cr molecular mass and T is absolute temperature (K). The decisive quantity is p_{Cr}, and its temperature dependence is being described by

$$p = 11.743\exp(-394000/RT) \qquad /\text{mbar}/ (6)$$

(R is the gas constant in $JK^{-1}mol^{-1}$)

2. *Chromium migration from the surface inwards into the specimen* expressed by the interdiffusion coefficient D:
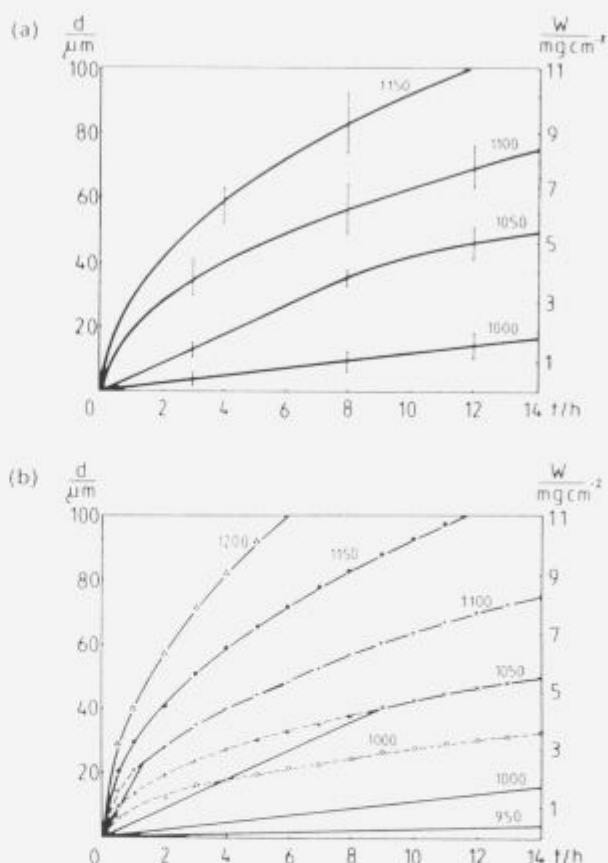
$$D = 2.08\exp(-243000/RT) \qquad (7)$$

Figure 6. Thickness of the chromized layer, d, and the mass increase, W, as a function of chromizing time t.
a) experimental results b) calculated values.
Slika 6. Debelina vakuumsko kromane plasti d in narastek teže W v odvisnosti od časa t a) eksperimentalni rezultati b) izračunane vrednosti.

By increasing the temperature T, p increases more rapidly than D as the evaporation enthalpy of chromium $\Delta H_{evap} = 394$ kJ mol^{-1} is higher than the activation energy for the diffusion $E_{dif} = 243$ kJ mol^{-1}. This circumstance leads to three different α-FeCr layer growth rates.

(a) At low temperatures $950 \leq \theta \leq 1050°C$ the slowest process is the Cr condensation. All condensed Cr atoms are transported immediately by diffusion from the surface inwards. Therefore the layer growth rate is linearly proportional to the condensation rate w:

$$w = Dt \quad \text{or} \quad d = Vwt$$

(b) At high temperatures $\theta \geq 1150°C$, when p is high enough, the slowest process is the diffusion, leading to the parabolic law

$$w = Dt \quad \text{or} \quad d = V\sqrt{2Dt}$$

Table 1. Values applied in the evaluation of the thickness, d, and weight increase, W, of α-FeCr layers given in Figure 6b. D-interdiffusion coefficient, p-equilibrium Cr vapour pressure, w-condensation rate of chromium, t_a, d_a—critical time coresponding α-FeCr layer thickness when the linear growth rate changes into the parabolic one.

°C	900	950	1000	1050	1100	1150	1200	1250
D $(cm^2 s^{-1})$	1.52×10^{-11}	4.20×10^{-11}	1.07×10^{-10}	2.56×10^{-10}	5.72×10^{-10}	1.21×10^{-9}	2.43×10^{-9}	4.65×10^{-9}
p (mbar)	1.0×10^{-7}	8.0×10^{-7}	3.8×10^{-6}	1.5×10^{-5}	5.7×10^{-5}	1.9×10^{-4}	5.9×10^{-4}	1.7×10^{-3}
W $(g cm^{-2} s^{-1})$	9.23×10^{-10}	7.24×10^{-9}	3.36×10^{-8}	1.35×10^{-7}	4.88×10^{-7}	1.62×10^{-6}	4.88×10^{-6}	1.36×10^{-5}
t_a (s)	4.32×10^7	1.94×10^6	2.3×10^5	3.4×10^4	5829	1150	247	59.31
(h)	1200	538.8	63.9	9.52	1.6	0.319	0.069	0.0165
d_a (μm^2)	362.4	127.60	70	41.9	25.8	16.6	10.9	7.3

At these values of T the linear rate appearing in the early stages of growth cannot, be detected.

(c) In the intermediate region $1050 \leq \theta \leq 1150°C$ the thickness of α-FeCr layer begins to increase linearly with time. The growth rate changes to a parabolic low at the critical time t, which corresponds to the critical thickness d.

The calculated growth rates of α-FeCr layers are shown in **Figure 6b.** **Table 1** contains all necessary data; p is obtained from the equation (6), w from the equation (5) assuming $\sigma = 1$, D from the equation (7), t_a and d_a from the relationships given in **Figure 6a.**
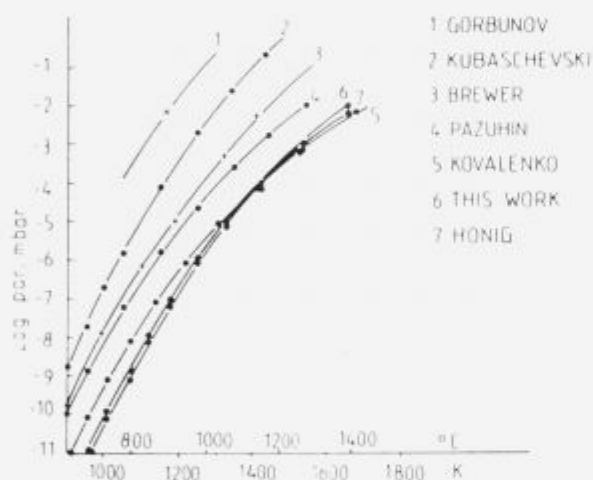

Figure 7. Temperature dependence of equilibrium Cr vapour pressure p according to various references[11-16].
Slika 7. Parni tlak kroma v odvisnosti od temperature po podatkih različnih avtorjev[11-16].

The real Cr vapour pressure p_{real} is equal to the equilibrium pressure p only if the experimental conditions are carefully chosen: $p_{RA} \leq 10^{-4}$ mbar, while the surface of the chromium granulate has to be as clean as possible and the ratio of specimens surface and the granulate amount must be adequate. If these conditions are not correctly chosen then p_{real} can be expressed by p multiplied by three correction coefficients $c_1, c_2, c_3 \leq 1$:

$$p_{real} = c_1 c_2 c_3 p \qquad (8)$$

where:

c_1 takes in account the portion of oxidized surface of granulate;

c_2 takes in account the residual atmosphere;
c_3 takes in account the surface/granulate ratio.

5 Conclusion

The results of this investigation show that none of CVD processes is suitable for the protection of iron parts for magnetic circuit in miniature hermetic relays. For this purpose PVD process of vacuum chromizing was developed. With this procedure the maximal chromium content of 15% Cr at the surface was obtained, enough for corrosion protection in corrosive media which are demanded by MIL-R-39016 and MIL-R-5757. PVD process assures the optimal magnetic properties, a very low coercivity and a good weldability and additionally, it is an environment friendly process.
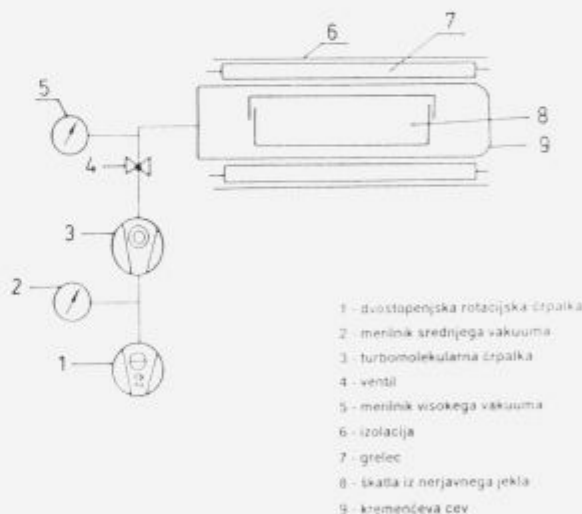

1 - dvostopenjska rotacijska črpalka
2 - merilnik srednjega vakuuma
3 - turbomolekularna črpalka
4 - ventil
5 - merilnik visokega vakuuma
6 - izolacija
7 - grelec
8 - škatla iz nerjavnega jekla
9 - kremenčeva cev

Figure 8. A schematic diagram of PVD—vacuum chromizing procedure[7].
Slika 8. Shematičen prikaz PVD—vakuumskega difuzijskega postopka kromanja.

6 References

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