Titanium diffusion coatings on austenitic steel obtained by the pack cementation method

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Abstract: The surface of specimens made of 316L austenitic steel was modified by titanium diffusion. The diffusion coatings were obtained by packing in a powder mixture consisting of titanium powder, NH_4Cl and Al_2O_3 powder. The procedure required high temperatures, over 900 °C, and long durations. Atomic titanium was formed in the muffle during the process. Titanium atoms from the metallic part surfaces diffuse towards the interior and a diffusion layer is formed as a function of the steel composition. Titanium diffusion into the surface of 316L austenitic steel determines the formation of a complex coating: a thin layer of TiN at the exterior and a layer consisting of compounds containing Ti, Ni and Fe in the interior of the coating. The obtained coatings were continuous, adherent and had a hardness higher than that of the substrate material. The diffusion coatings were investigated by optical and electron microscopy, X-ray diffraction and Vickers microhardness tests.

Keywords: titanium diffusion coatings on 316L austenitic steel; pack cementation method.

INTRODUCTION

In addition to a very broad field of other applications, 316L austenitic steel with a high content of chromium (16–18 wt. %) and nickel (10–14 wt. %)[1] is employed for the manufacture of bone implants, such as hip, knee and femur prostheses. This type of steel is well tolerated by the human organism but after a long period of time in contact with human fluids metallic ions leach from the prostheses. It has been proved that hexavalent chromium ions are very toxic or even cancerous.[2,3] Such a drawback can be overcome if the surface of the implant is coated with a biovitroceramic layer. The biovitroceramic material previously stu-

died[4,5] possessed a thermal dilatation coefficient much lower than that of 316L austenitic steel and close to that of TiN ($\alpha = 90{\times}10^{-7}$ °C^{-1}).[6]

In order to achieve a better adherence between the previously studied biovitroceramic and the steel, the thermal dilatation coefficients of the two materials have to be as similar to each other as possible. This can be achieved by modifying the composition and the surface structure of samples made of 316L austenitic steel by diffusion layers. As a function of covering elements and substrate material, the surface layers obtained by diffusion processes can be of the solid solution type with wide miscibility domains or, otherwise, a sequence of phases can be formed progressively according to the equilibrium diagrams. Two concurrent diffusion processes occur, *i.e.*, the diffusion of the covering element or elements towards the bulk of the metallic substrate is accompanied by the diffusion towards the surface of elements from the substrate material. Within the layer, the mass transport is characterized by the diffusion coefficients, while layer increase occurs according to kinetic laws specific to each phase.[7] Formation of these layers offers several advantages, *i.e.*, very good adherence to the substrate, chemical and mechanical properties superior to those of the substrate material and only minimal dimensional changes occur. There are several methods for obtaining diffusion layers. The one employed in this work, much studied in previous papers, is that of powder packing using ammonium chloride as an activator.[8–10] Using the pack cementation method, diffusion coatings with different elements, Cr,[11–13] V,[13,14] Al,[15–17] B,[18] Cr–V,[12,13,19] Al–Cr,[20–22] Cr–Si,[23,24] and Ti,[25–28] can be obtained.

Diffusion layers are formed in two different stages. In the first stage, the diffusive element is brought in contact with the surface of the substrate material and in the second one, the diffusion process which follows consists of the gradual adsorption of the diffusive element into the base material network of the substrate. In the case of the powder mixture packing method with NH_4Cl as the activator, the diffusive element is formed as a result of a chemical reaction in the gaseous state. In general, the mechanism for supplying the diffusive element is as follows. The gaseous phase consists of halides, especially chlorides. Several types of reactions can occur in which a BX_2 halide of a metal frees the diffusive element B so that it can diffuse into the substrate metal A. These reactions can be represented schematically as:[10]

Change reaction:

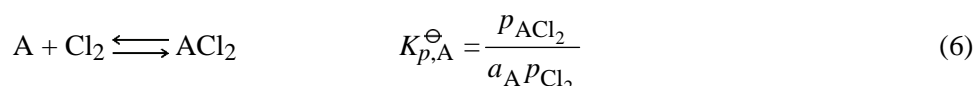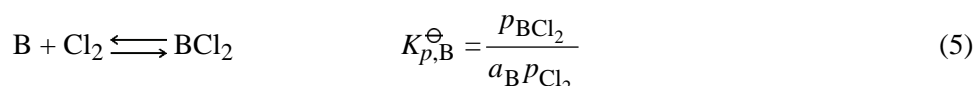$$A + BX_{2(g)} \Longleftrightarrow AX_2 + B \tag{1}$$

Reducing reaction:

$$BX_{2(g)} + H_2 \Longleftrightarrow 2HX + B \tag{2}$$
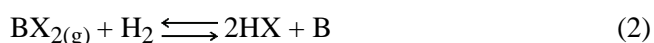
Thermal decomposition reaction:

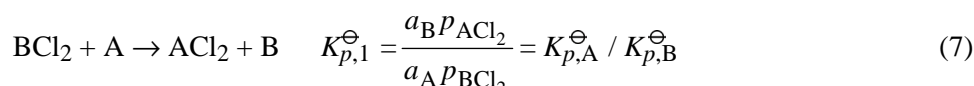$$BX_2 \rightarrow B + X_2 \tag{3}$$

The change reaction implies the removal or displacement of an A atom from the surface of the base material for each deposited B atom. For A and B atoms with similar atomic masses, this reaction produces only minimal changes of the sample weight regardless of the thickness of the diffusion layer. The other two reactions lead to a weight increase of the treated material. The possibility for these reactions to occur can be inferred from some thermodynamic considerations. The concentration of the B element deposited on the metallic substrate A depends on the partial pressure of the gaseous compounds at the treatment temperature, P_i, and activities, a_i, of both the deposited material B and the base metal A. If the equilibrium condition for free energy, $\Delta G^{\ominus}$, is applied:

$$\Delta G^{\ominus} = -2.303RT \log K_p^{\ominus} \tag{4}$$

for the formation of BCl_2 and ACl_2 halides, reactions (5) and (6), then the equilibrium constants, $K_p^{\ominus}$, are:

$$B + Cl_2 \rightleftharpoons BCl_2 \qquad\qquad K_{p,B}^{\ominus} = \frac{p_{BCl_2}}{a_B p_{Cl_2}} \tag{5}$$

$$A + Cl_2 \rightleftharpoons ACl_2 \qquad\qquad K_{p,A}^{\ominus} = \frac{p_{ACl_2}}{a_A p_{Cl_2}} \tag{6}$$

and for the interchange reaction (1):

$$BCl_2 + A \rightarrow ACl_2 + B \qquad K_{p,1}^{\ominus} = \frac{a_B p_{ACl_2}}{a_A p_{BCl_2}} = K_{p,A}^{\ominus} / K_{p,B}^{\ominus} \tag{7}$$

$$\text{Log } K_{p,1}^{\ominus} = \log K_{p,A}^{\ominus} - \log K_{p,B}^{\ominus} \tag{8}$$

For layers where $a_A \approx a_B$ at the surface, a difference of –1 units in equation (8) means that $\approx$ 10 % of the metal chloride vapors are converted into the covering metal in an atomic state. A difference of –2 units represents a conversion of $\approx$ 1 %, which is the minimum for a practical interchange reaction.[10]

The goal of this work was to obtain titanium diffusion layers on the surface of 316L austenitic steel specimens by the pack cementation procedure. The diffusion layers obtained in this manner modify the surface properties of the steel.

EXPERIMENTAL

The 316L austenitic steel samples used as substrates were in the form of small plates with dimensions of 10 mm×10 mm×3 mm. The chemical composition of 316L steel is given in Table I. Prior to the thermochemical treatment, all the plates were ground on a set of 240–280 mesh emery papers and degreased in acetone. There were weighted before and after the treatment with a precision to the fourth decimal (10^{-4} g).

The powder mixtures consisted of the following substances: 99.9 % (Merck purity) titanium powder with a 150 µm granulation, 99.5 % aluminum oxide with a 125 µm granulation and p. a. ammonium chloride. The ammonium chloride was dehydrated and finely ground be-

fore preparation of the mixtures. 3 wt. % NH_4Cl was used in all the experiments. The titanium and aluminum oxide powders were employed in various concentrations. The working conditions for the sample treatment are shown in Table II.

TABLE I. Composition and thermal dilatation coefficients of 316L austenitic steel

Composition	C	Cr	Ni	Mn	Mo	Si	P	S	N	Fe
wt. %	0.03	16–18	10–14	2.0	2–3	0.75	0.045	0.03	0.10	Up to 100
Thermal dilatation coefficient, $\alpha \times 10^7$ / °C^{-1}					159 (0–100 °C) 162 (0–315 °C) 175 (0–538 °C)					

TABLE II. Working conditions for different treatments

Powder mixture composition, wt. %			t / °C	τ / h
Ti	Al_2O_3	NH_4Cl		
77	20	3	1000; 1125; 1150; 1200	2; 5; 7.5

Powder mixtures together with the samples were placed in refractory steel crucibles with a 25 mm diameter and 50 mm height. Only one sample, placed exactly in the middle of the crucible, was treated at a time. The powder mixture was compacted carefully around the sample so that the latter was uniformly covered. The crucible was filled up to the upper end, covered with a metallic lid and placed in a ceramic crucible in order to protect the ceramic wall of the furnace. A L-1206 M type furnace with a horizontal hearth and a Kanthal electrical resistance provided with a Chromel–Alumel thermocouple with a precision of the maintaining the temperature in a stability regime of ±2 °C was employed.

After treatment, the samples were cleaned, degreased in acetone and prepared for examination. They were mounted in methacrylate in the cross section and ground on 240–1200 mesh emery papers and a felt impregnated with Al_2O_3 emulsion (0.75 and 0.25 µm). The surfaces prepared in such a manner were etched with Vilella reagent (1.0 g picric acid, 5.0 cm^3 concentrated HCl and 95 cm^3 ethanol).

Optical microphotographs were taken by means of an optical M.C.1.M. microscope provided with an Exacta Vares camera.

An SEM Hitachi-S 2600 instrument equipped with a dispersive energy spectroscope (EDS) was used for qualitative and quantitative analysis. Images of secondary electrons (SEM) and XKα-rays for Ti, Cr, Ni and Fe were obtained.

In order to identify the phases and compounds formed within the diffusion layer, the samples were examined by X-ray diffraction with a DRON-20 instrument using CuKα1 radiation (λ = 1.54178 Å).

Vickers microhardness values of both the layer and the metal substrate were measured with a Hannemann hardness meter provided with a diamond pyramid with an angle of 136° between the facets[29] and calculated using the Relation:

$$HV_P = 1854.4 \frac{P}{\varepsilon^2 d^2} \tag{9}$$

where P is the penetration force (in the present case, P = 100 gf), ε is a transforming factor (a micrometric division is equal to 0.2907 µm) and d represents the number of micrometric divisions corresponding to the microhardness indent diagonal. The values of the Vickers microhardness, HV_P, are expressed in Kgf/mm^2.

RESULTS AND DISCUSSION

The samples titanized under conditions when the powder mixture contained 77 wt. % titanium and treated at temperatures of 1000, 1150 and 1200 °C for 5 h are shown in Figs. 1–3, respectively. The diffusion layers were continuous, uniform, very adherent to the metallic substrate and had a thickness between 30 and 350 µm.
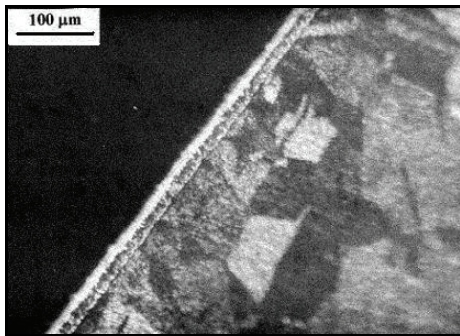

Fig. 1. Optical microphotograph of a cross section of a sample titanized in a powder mixture with 77 wt. % Ti at 1000 °C for 5 h; Vilella metallographic etchant.
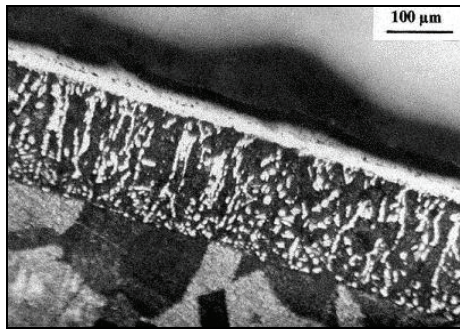
Fig. 2. Optical microphotograph of a cross section of a sample titanized in a powder mixture with 77 wt. % Ti at 1150 °C for 5 h; Vilella metallographic etchant.
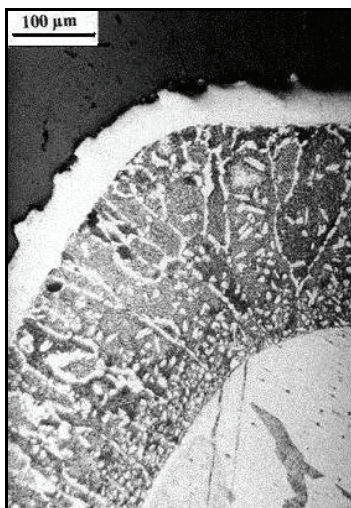

Fig. 3. Optical microphotograph of a cross section of a sample titanized in a powder mixture with 77 wt. % Ti at 1200 °C for 5 h; Vilella metallographic etchant.

The variation of the layer thickness with temperature is shown in Fig. 4, from which it can be seen that the variation follows an exponential law typical for a diffusion process. The variation of the layer thickness with time at a constant temperature, 1000 °C, follows a parabolic law, as can be seen from Fig. 5, this being another proof for the fact that the layers formed with the participation of a diffusion process.
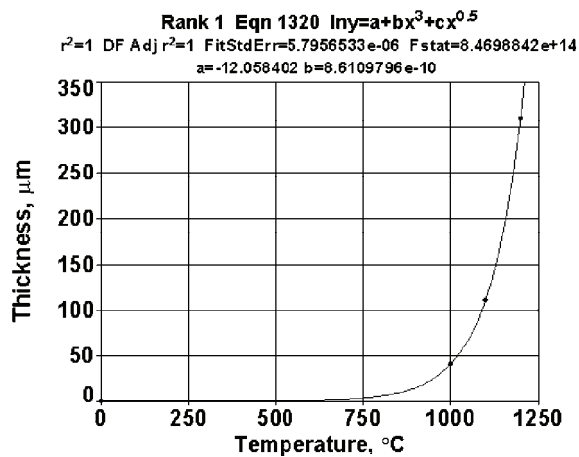

Rank 1 Eqn 1320 lny=a+bx^3+cx$^{0.5}$
r^2=1 DF Adj r^2=1 FitStdErr=5.7956533e-06 Fstat=8.4698842e+14
a=-12.056402 b=8.6109796e-10

Fig. 4. Variation of the layer thickness with temperature (diffusion time 5 h; 77 wt. % Ti).

Rank 2 Eqn 8104 [Form2_] y=a(1-1/(1+abx))
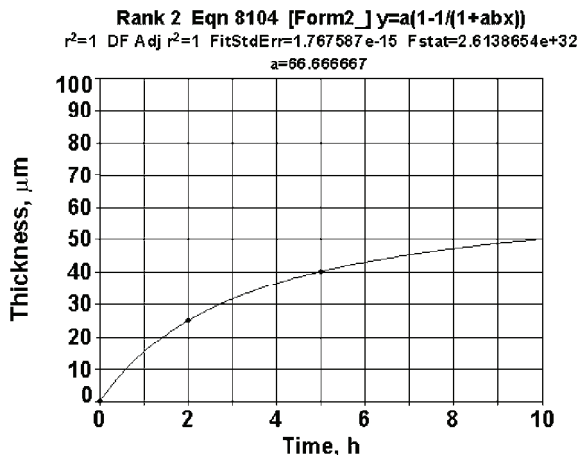r^2=1 DF Adj r^2=1 FitStdErr=1.767587e-15 Fstat=2.6138654e+32
a=66.666667

Fig. 5. Variation of the layer thickness with time (temperature 1000 °C; 77 wt. % Ti).

Vickers microhardness measurements are listed in Table III. The indent size on the layers was much smaller than that on the austenitic steel substrate (Fig. 6).

The distribution of titanium within the layer and the main elements, Cr, Ni and Fe, that underwent thermochemical treatment of the sample at 1150 °C for 5 h was well evidenced by SEM and EDS (Figs. 7–11).

From Fig. 7, it can be seen that titanium diffused not only into the coating, but, in a lower concentration, also into the substrate.

TABLE III. Vickers microhardness (average of at least 5 measurements) of different layers and substrate (77 wt. % Ti; 1200 °C; 5 h)

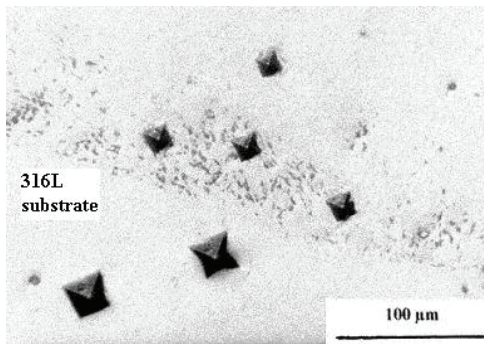| Zone	HV_P / Kgf mm^{-2} (P = 100 gf)
Layer (exterior zone, thin, light color)	849
Layer (interior zone, thicker)	475
Substrate of 316L austenitic steel	158
Untreated 316L austenitic steel	203

Fig. 6. Vickers microhardness imprints on a cross section coating–substrate, penetration force P = 100 gf (77 wt. % Ti; 1200 °C; 5h).
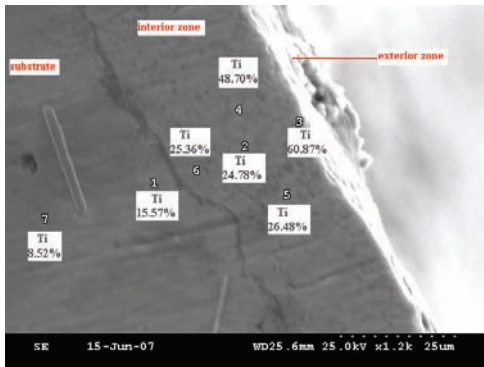

Fig. 7. SEM Secondary electron image of a cross section of a sample titanized in a powder mixture with 77 wt. % Ti at 1150 °C for 5 h.
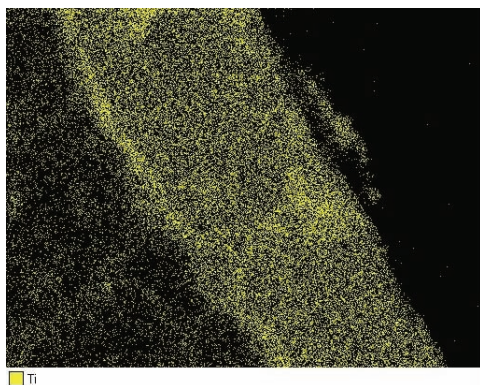

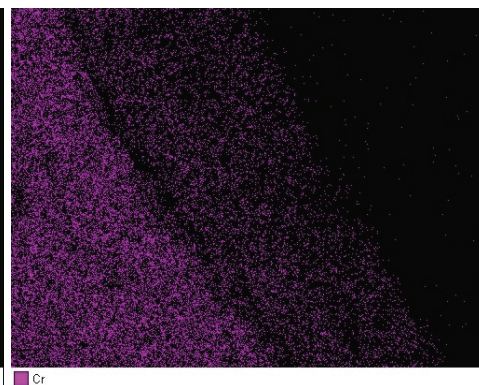Fig. 8. Image of X- ray KαTi; ×1200; (77 wt. % Ti; 1150 °C; 5h).

Fig. 9. Image of X- ray KαCr; ×1200; (77 wt. % Ti; 1150 °C; 5h).
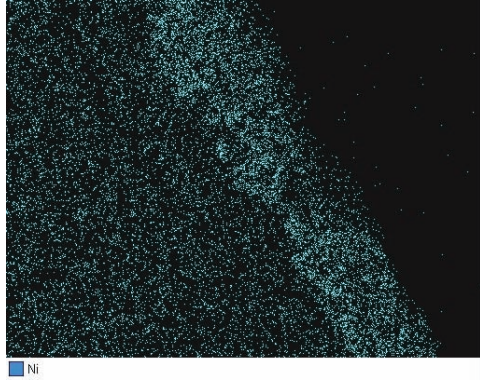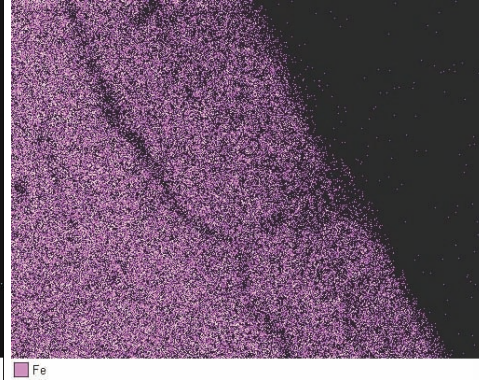
Fig.10. Image of X- ray KαNi; ×1200;
(77 wt. % Ti; 1150 °C; 5h).

Fig. 11. Image of X- ray KαFe; ×1200;
(77 wt. % Ti; 1150 °C; 5h).

It may be seen by examining Figs. 8 and 9 that titanium almost replaced chromium in the coating. Figure 10 shows that nickel concentrates in the inner layer. The distributions of iron in the coating and substrate do not differ significantly (Fig. 11).

The X-ray diffraction analysis of the surfaces of the samples proved the formation of the TiN compound (Fig. 12), a fact that is in concordance with the high Vickers hardness value, $HV_{P = 100 \text{ gf}}$ = 849 Kgf/mm^2, obtained for the exterior layer which was formed by diffusion with the reaction process. The TiN compound was distributed into the matrix of the layer. If the exterior layer would be formed only of the TiN compound, it would be thinner and much harder. The inner layer is much thicker and possesses a Vickers hardness lower than that of the outer one, but higher than that of the metallic substrate (Table III). The value of the hardness was constant through the entire thickness of the inner layer. This fact proved that this layer was formed also by diffusion with the reaction process.
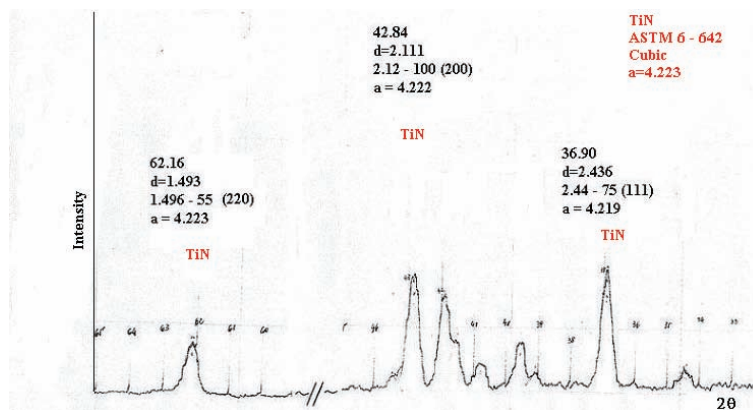

Figure 12. Diffractogram of the exterior layer of a sample titanized at 1150 °C for 5 h;
77 wt. % Ti. (*d* and *a* in Å).

The nature of the compound was different from that in the outer layer. By corroborating the data of the optical micrograph (Fig. 2), electron micrographs (Figs. 8–11) and the microhardness measurements (Fig. 6), it was concluded that the interior layer is formed of a Ti–Ni–Fe compound.

CONCLUSIONS

1. Specimens of 316L austenitic steel used in implantology for manufacturing prostheses were subjected to thermochemical treatment by titanium diffusion in order to obtain surface coatings.

2. As a function of the variation of the process parameters, temperature and duration, diffusion layers with a thickness between 30 and 350 μm were obtained.

3. All coatings obtained at temperatures higher than 900 °C consisted of two zones:

– an exterior zone, thin and lightly colored, formed of TiN and with a hardness approximately 5 times higher than that of the metallic substrate;

– a thicker inner zone formed of a Ti–Ni–Fe compound. The hardness value of this layer was approximately 3 times higher than that of the metallic substrate with the constant value throughout the whole thickness.

ИЗВОД

ПРЕВЛАКЕ НА АУСТЕНИТНОМ ЧЕЛИКУ НАСТАЛЕ ДИФУЗИЈОМ ТИТАНА ПАКУЈУЋОМ ЦЕМЕНТАЦИЈОМ

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Површина узорака аустенитног челика 316L модификована је дифузијом титана. Превлаке настале дифузијом добијене су паковањем из смеше прахова која се састојала од прахова титана, NH_4Cl and Al_2O_3. Процедура је дуготрајна и захтева високе темературе, преко 900 °C. На почетку процеса формира се атомски титан. Атоми титана дифундују из металних делова површине ка унутрашњости, чиме се формира дифузиони слој у зависности од састава челика. Дифузија титана у површину аустенитног челика одређује формирање комплексне превлаке: танак слој TiN у површинским деловима превлаке и слој у унутрашњости превлаке који се састоји од једињења која садрже Ti, Ni и Fe. Добијене превлаке су континуалне, добро пријањајуће и тврдоће која је већа од оне коју има материјал подлоге. Дифузионе превлаке су испитиване оптичком и електронском микроскопијом, дифракцијом x-зрака и Vickers-овим тестом микротврдоће.

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