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Surface modification by solid phase titanium diffusion of a 316L austenitic steel

M. BRITCHI*, N. ENE, M. OLTEANU, C. RADOVICI
Romanian Academy, Institute of Physical Chemistry "Ilie Murgulescu"
ICECHIM Splaiul Independentei 202, sector 6, Bucharest, ROMANIA

Surface modification of austenitic steels with high Cr and Ni contents was performed in order to obtain titanium-containing diffusion layers. The steel we employed was 316L type used in implantology with a composition: C=0.03; Cr=16-18; Ni=10-14; Mo=2-3; Mn=2.0; Si=0.75; P=0.045; S=0.03 and N=0.10, in % weight. The diffusion layers were prepared following a thermo-chemical treatment that implied a powder packing procedure. The packing mixture was made of titanium powder of different proportions, aluminium oxide and ammonium chloride of concentration up to 3 % in weight. Working temperature and time were varied. Solid phase diffusion layers need high temperature, over 900ºC and long time period, many hours. The main advantage of titanizing by powder packing procedure is that the layer is an alloy type and is very uniform no matter the shape and the roughness. Diffusion layers obtained under different temperature and treatment duration conditions were investigated on their cross sections by optical microscopy and Vickers microhardness trials. The nature of the different phases formed in the diffusion coatings were investigated by X-ray diffraction. By surface modification of the metallic parts made of 316L austenitic steel, we followed two objectives: (i) to increase the corrosion resistance, knowing the fact that implants manufactured from such steel present a certain degree of leaching which leads to expelling extremely toxic chromium ions into the organism and (ii) to prepare the surface such as to be proper for the covering with biovitroceramic coatings.

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1. Introduction

The 316L austenitic steel with high chromium (16-18 % in weight) and nickel (10-14 % in weight) contents is usually used for making of big bone implants such as hip and femur prostheses. This steel is well tolerated by the human body but after a long contact of the metallic prosthesis with the body fluids some leaching of the alloy ions into the human fluids occurs. It has been proved that chromium hexavalent ions are even carcinogenic [1]. Such an inconvenient can be surpassed by covering the metallic substrate with a titanium-containing diffusion layer.

As a function of covering elements and the elements of the substrate material, the surface layers obtained by diffusion processes can be of solid solution type with wide miscibility domains, or they can form progressively a succession of phases according to the phase diagrams. In the latest case, the diffusion elements atoms pass through all formed phases before reaching the metallic substrate. The diffusion of the covering elements towards the bulk of a metallic part is accompanied by a diffusion of the substrate elements towards the surface. Within the layer, the mass transport is characterized by diffusion coefficients and the layer building takes place according to kinetic laws appropriate to each phase [2]. Through obtaining of the diffusion layers we follow to modify the surface of the metallic parts. These layers present several advantages: have a very good adherence to the substrate and chemical and mechanical properties better than those of the substrate material and they also determine minimal dimensional changes.

There are several methods for obtaining diffusion layers. The method we employed was the one largely used and presented in our previous works [3-8], namely, packing in powder containing as activator NH_4Cl.

2. Experimental

The diffusion layers are formed as a result of at least two distinct processes. The first one consists in bringing the diffusive metal in contact with the surface of the base material followed by the proper diffusion process which consists in a progressive adsorption of the diffusive element within the base material network. In the case of the method of powder mixture containing NH_4Cl as activator, diffusive element arises from the gaseous phase. The mechanism for supplying the diffusive element is the following. The gaseous phase is generally made of halogen compounds, specially, chlorides. Several types of reactions can take place by which halide, BX_2, of a metal releases the diffusive metal, B, which diffuses within the substrate metal A. These reactions can be schematically represented as such [9]:

Change reaction:

$$A + BX_{2\ (gas)} \leftrightarrow AX_2 + B \qquad (1)$$

Reduction reaction:

$$BX_{2\ (gas)} + H_2 \leftrightarrow 2HX + B \qquad (2)$$

Thermal decomposition reaction:

$$BX_2 \rightarrow B + X_2 \qquad (3)$$

The change reaction implies either removing or displacing an atom A from the surface of the base material for each deposited B atom. In the case when atoms A and B have close atomic masses, the reaction produces minimal changes in the metallic part weight, no matter the thickness of the diffusion layer. The other two reactions lead to a weight increase of the treated metal.

The possibility of producing these reactions can be deduced from thermodynamic considerations. Thus, the concentration of element B deposited on the substrate A surface depends on both, partial pressure of the gaseous components at the treatment working temperature and activity of the deposited metal B against the base metal.
If the equilibrium condition of free energy

$$\Delta G^0 = - 2.303\ RT \log K_P \qquad (4)$$

If it is applied in the case of formation of BCl_2 and ACl_2, reactions (5) and (6), the equilibrium constants, K_P are:

$$B + Cl_2 \leftrightarrow BCl_2 \qquad K_{P,B} = \frac{P_{BCl_2}}{a_B P_{Cl_2}} \qquad (5)$$

$$A + Cl_2 \leftrightarrow ACl_2 \qquad K_{P,A} = \frac{P_{ACl_2}}{a_A P_{Cl_2}} \qquad (6)$$

For the change reaction (1)

$$K_{P,1} = \frac{a_B P_{ACl_2}}{P_{BCl_2} a_A} = \frac{K_{P,A}}{K_{P,B}} \qquad (7)$$

$$\log K_{P,1} = \log K_{P,A} - \log K_{P,B} \qquad (8)$$

For layers where $a_A \approx a_B$ on the surface, a difference of -1 unit in equation (8) means that ~ 10 % of the vapours of the solute metal chloride are converted into the covering metal in an atomic state. A difference of – 2 units represents a 1 % conversion which can constitute a necessary minimum for a practical interchange reaction.

For the present study, we used powder mixtures made of: titanium powder of several granulations and concentrations of up to 77 % in weight, aluminum oxide powder and ammonium chloride up to 3 % in weight. Under the mostly used conditions for diffusion metallizing, the gaseous phase is generated directly inside the working enclosure by NH_4Cl decomposition at temperatures over 800ºC:

$$2NH_4Cl \rightarrow N_2 + 3H_2 + 2HCl \qquad (9)$$

The formed gases react with the metals from the powder mixtures to form chlorides which subsequently free the diffusive element in atomic state (titanium atom in our case), by one of the described mechanisms (change, reducing, thermal decomposition reactions) or in the most cases, by more types of reactions to participate. Diffusion can occur with formation of a solid solution by a physical mechanism or formation of compounds by diffusion with reaction mechanism, a case when the chemical activities play an important role.

The experiments were carried out in an electrical furnace with a vertical ceramic hearth. The samples were packed in either metallic or ceramic cells with dimensions: ϕ = 2, 3 and 4 cm and height h = 5.5 cm. Retorts were tightly closed with lids. The process was conducted in air. The 316L austenitic steel parts had the dimensions 10 x 10 x 3 mm. Some plates were polished on 240 – 280 mesh grinding papers and others were sandblasted with Al_2O_3 powder (125 μm). Before being packed in the powder mixtures, the plates were degreased with acetone. After the treatment the plate were cleaned, and secured in Duracryl in a cross section and polished on a set of grinding papers as well as on felt soaked with Al_2O_3 (0.25 μm) emulsion. Thus prepared samples were then etched with a reactive Vilella and examined by means of an optical microscope in order to obtain micrographs.

Vickers microhardness was made with a Hannemann instrument provided with a diamond prism, on the cross sections of the samples without etching. The imprint force, P, was 100 gf.

In order to identify the formed phases and compounds, the samples were examined by X-ray diffraction with DRON-20 diffractometer at $CuK_{\alpha1,\ \alpha2}$ (λ = 1.54178 Å) radiation.

3. Results

The austenitic steel 316L of the samples has the following composition: C=0.03; **Cr=16-18**; **Ni=10-14**; Mn=2.0; Mo=2-3; Si=0.75; P=0.045; S=0.03; N=0.10 and Fe up to 100% in weight.

The working conditions for titanizing treatments are listed in Table 1.

Table 1. Working conditions.

Composition of powder mixture, (% in weight)			Temp. (ºC)	Time (h)
Ti	Al_2O_3	NH_4Cl		
77	20	3	1000; 1125; 1150; 1200	2; 5
50	47	3	1000	5
25	72	3	1000	5

The samples titanized with a powder mixture containing 77% titanium (Merck purity and 150 μm) at temperature higher than 1000ºC displayed very uniform layers which follow strictly the sample contours, *Figures 1-3.*

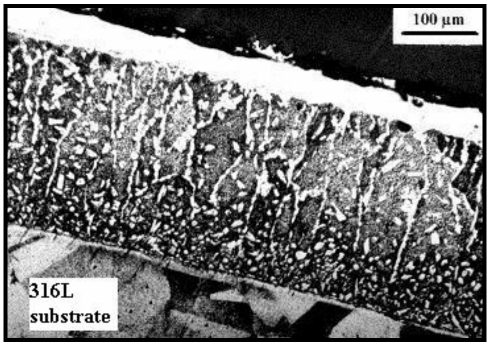


Fig. 1. Optical micrograph of a cross section of a sample titanized in a powder mixture with 77 % Ti in weight; ***1200ºC****; 5h; metalographic etching with Vilella reactive.*

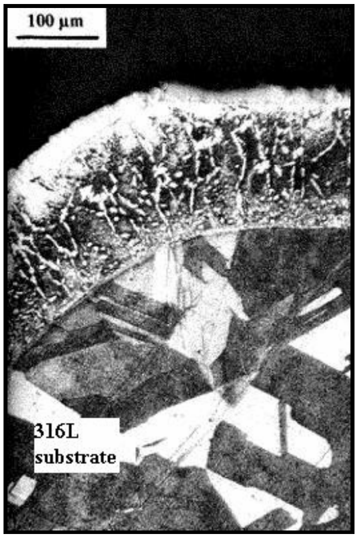


Fig. 2. Optical micrograph of a cross section of a sample titanized under the following conditions: 77 % Ti powder, in weight; ***1200 ºC****; 2h; metallographic etching with Vilella reactive.*

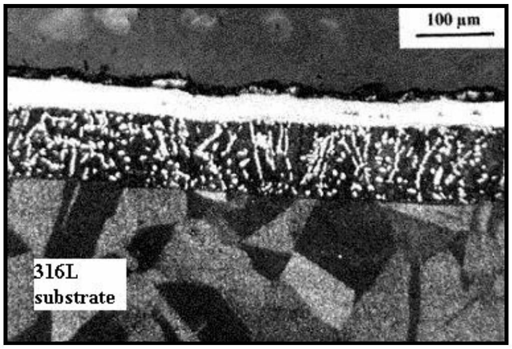


Fig. 3. Optical micrograph of a cross section of a sample titanized under the following conditions: 77 % Ti powder, in weight;; 1125ºC; 5h; metallographic etching with Vilella reactive.

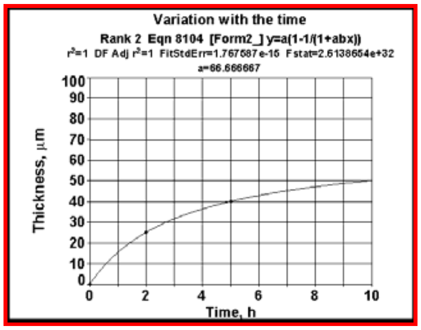


Fig. 4. Variation in time of the diffusion layer thickness (temperature of ***1000ºC****)*

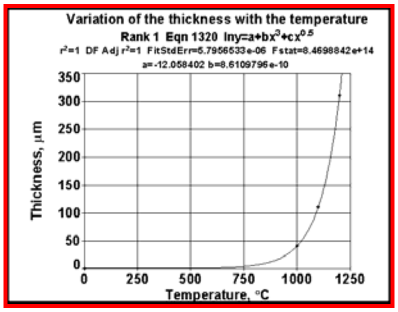
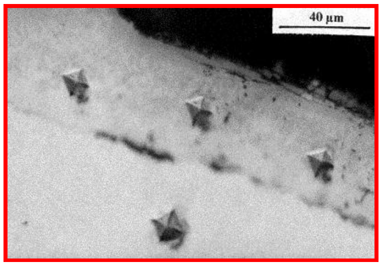
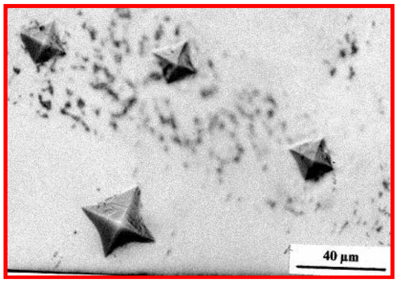


Fig. 5. Layer thickness variation with temperature (diffusion time: 5h).

Layer thickness follow a parabolic type time variation and , *Fig. 4*, and an exponential one with temperature, *Fig. 5*, fact that confirm the diffusive character of the treatment.



outer zone of the layer →



inner zone of the layer→

substrate→

Fig. 6. Optical micrograph of a cross section of a sample titanized under the following conditions: 77 % Ti powder, in weight; ***1200ºC****; 5h; without metallographic etching; Vickers microhardness imprints at P=100 gf.*

Vickers microhardness trials provided the values listed in *Table 2.*

Table 2. Vickers microhardness values.

Zone	Vickers microhardness, $HV_{(P=100\ gf)} \rightarrow Kgf/mm^2$
Layer (upper zone, thin, bright colour, TiN)	849
Layer (interior zone, thicker)	475
316L austenitic steel substrate	158
Untreated 316L austenitic steel	203

4. Discussion

Titanium diffusion onto the 316L austenitic steel surface led to diffusion layers with thicknesses between 140 and 340 μm as a function of temperature and treatment duration. By examining the optical micrographs, *Figures 1-3*, one can observe that layers are formed of two zones: an outer one which is thin, bright and well delimited and an inner, much larger one. Microhardness trials gave different values, that is, Vickers microhardness was much greater ($HV_{P=100\ gf)}$ = 849 Kgf/mm^2), for the outer zone than that for the substrate microhardness ($HV_{P=100\ gf)}$ = 158 Kgf/mm^2). The microhardness of the inner zone was 3 times higher than that of the substrate, *Table 2,* and remained constant on all thickness of the inner layer. This fact is a proof that the layer was formed by diffusion with reaction mechanism. The nature of the outer zone was determined by X-ray diffraction analysis. Thus, the outer zone is formed of TiN, *Fig. 7.*

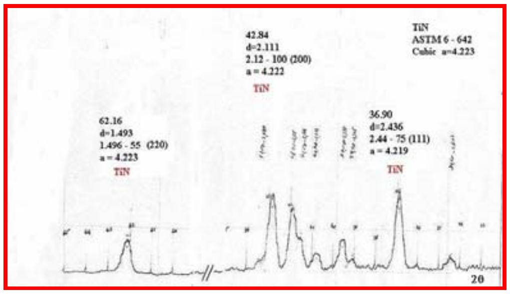


Fig. 7. Diffractograme of the diffusion layer on the surface of a sample of 316L austenitic steel titanized at ***1150 ºC****, 5h.*

In another paper we shall determine the nature of the inner layer, by X-ray diffraction, after removing the outer layer by polishing.

Because the diffusion layers are obtained at high temperatures, over 900ºC, and treatment durations of hours, the steel structure modified as the grain dimmensions increase and therefore a decrease of microhardness is registred. The microhardness of non-treated 316L austenitic steel was $HV_{P=100\ gf}$ = 203 Kgf/mm^2, while the substrate microhardness after termochemical treatment was $HV_{P=100\ gf}$ = 158 Kgf/mm^2

5. Conclusions

1. Parts of 316L austenitic steel used for prostheses in implantology were thermochemically treated by titanium diffusion onto surface.

2. The method used was powder packing with NH_4Cl as activator.

3. Diffusion layers with thickness between 140 and 340 μm were obtained as a function of the treatment parameters: titanium powder amount, temperature and process duration.

4. All layers obtained at a temperature higher than 900ºC were constituted of two zones. The outer zone constituted by TiN is thinner, bright and has a microhardness of ~ 5 times higher than the substrate.

6. We followed two goals in an attempt to modify the surface of 316L austenitic steel with the layers obtained by titanium diffusion:

- increasing of the corrosion resistance against the human body fluids
- obtaining a surface to adhere better onto a biovitroceramic material having in composition: SiO_2-Na_2O-K_2O-Li_2O-CaO-MgO-P_2O_5-B_2O_3-TiO_2, applied by enameling.

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[*] Corresponding author: iuliab40@yahoo.com