Obtaining biocompatibile protective coatings on titanium alloys to artificial medical instrument

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Titanium is a metal that has been used in various and varied medical applications for about 40 years. Titanium and its alloys have excellent corrosion resistance, in many aqueous media, and assure their excellent biocompatibility. A variety of surface modification processes have been proposed for titanium alloys. The new method of creation biocompatible layers on titanium-aluminium alloys that we want to investigate is based on the use of ascending diffusion effect of solute atoms at sputtering of metal-solvent surface by inert gases ions. Using theoretical calculations technique described, it is possible to choose modes for carrying out ion-plasma processing aimed at getting the effect of ascending diffusion in titanium-aluminium alloy.

Keywords and phrases: biocompatibility, segregation, ascending diffusion, ion-plasma processing, biocompatible layers.

The problem of materials incompatibility to artificial and medical instrument predetermines the large necessity of modern medicine to develop new protective coatings with the wide range of functional properties. For this reason it is important to search for methods of obtaining biocompatibile coatings with high durability and adhesion.

Titanium is a metal that has been used in various and varied medical applications for about 40 years. Although many biomaterials have come and gone during this period, titanium is one of the few that has seen its uses and reputation enhanced over the years [1].

More than 1000 tonnes (2.2 million pounds) of titanium devices of every description and function are implanted in patients worldwide every year. Requirements for joint replacement continue to grow as people live longer or damage themselves more by intensive sports training or jogging, or are seriously injured in road traffic and other accidents.

It can be explained by excellent mechanical properties, considerable strength, low weight, outstanding corrosion resistance possessed by titanium and titanium alloys and have led to a wide and diversified range of successful applications which demand high levels of reliable performance in surgery and medicine as well as in aerospace, automotive, chemical plant, power generation, oil and gas extraction, sports, and other major industries. The range of available titanium alloys enables designers of medical devices to select materials and forms closely tailored to the needs of the application.

Although pure titanium is a highly reactive metal it is usually protected by the presence of a very stable, self-healing passive oxide film consisting mainly of TiO_2. It is this film which is responsible for excellent corrosion resistance of titanium and its alloys, in many aqueous media, and assures their excellent biocompatibility. However, following revision surgery, after several years of use, concerns were raised regarding the creation of unwanted, titanium based debris (particles). Such debris is produced as a result of the combined actions of corrosion and wear (corrosion–wear). The possibility of toxic effects has also been reported. Consequently, there is great interest in overcoming the poor corrosive-wear resistance of titanium alloys through appropriate surface engineering. A variety of surface modification processes have been proposed for titanium alloys. These are in various stages of development. In corrosion–wear, it is very important to consider the synergy between corrosion and wear; wear is increased by the action of corrosion and corrosion increased by the action of wear [2].

One method of improving the resistance of titanium to abrasion is ion implantation into its surface. This technique allows one to improve the fatigue and tribological properties of metallic materials. The literature on the subject provides many reports on the improvement in the anticorrosion and tribological properties of materials subjected to ion implantation. In titanium alloys these properties can be improved by implanting ions of nitrogen or carbon. In the literature we can find many descriptions of how nitrogen ions implanted into the surface of titanium alloys affect the tribological properties of these materials [3].

Another methods are an oxygen diffusion hardening process called "thermal oxidation" (TO) and arc ion plating (AIP). This and a lot of other techniques of surface treatment provide satisfactory hardness and corrosion resistance but they don't provide sufficient adhesion.

The new method of creation of biocompatible layers on titanium-aluminium alloys that we want to investigate is based on the use of ascending diffusion effect of solute atoms at sputtering of metal-solvent surface by inert gases ions. In the process of ion sputtering the solute atoms move from deep regions to the surface and form thin layers in which the concentration of solute atoms can arrive at 80–100%. These layers have ever-higher adhesion to basic material. A transitional area appears where properties fluently change from a depth to the surface. Subsequent of superficial layers result in oxide formations which also have large adhesion to the metal--solvent.

The problem of structural defect initiation in materials that are submitted to the influence of different surface treatment is very important. Knowing the character of its formation can give an opportunity to obtain materials with pre-planned behaviour [4].

Segregation defects appearance due to the fact that ascending diffusion is caused not only by difference in atom volumes, constructing substitutional solid solution, but also by partial element diffusion coefficients.

The matter of kinetic diffusion segregation is easy to explain based on the simple example of two-component disordered substitutional solid solution, where diffusion is carried out by vacancy action. In this case the atom floe of both types (J_A J_B) and vacancies (J_V) is related by equation:

$$J_A + J_B + J_V = 0 \qquad (1)$$

which means that diffusion is carried out by vacancies under the constant number of lattice points.

Each time when due to any reason a directed vacancy flow J_V is maintained in the alloy, partial atom flows J_A and J_B are oriented in the opposite direction. Directed diffusion vacancy flow maintains some efficient force (generalized force of kinetic origin) that has to create ascending flows and, consequently, diffusion atom segregation. In the areas of vacancy source should segregate the atoms having higher partial diffusion coefficient, and in the areas of vacancy sinks — the atoms having lover partial diffusion coefficient.

Diffusion segregation may be illustrated by many effects where the necessary directed vacancy flow is supported either by the surface curvature or by the difference of structural state of the parts that comprise a diffusion pair. From the whole variety of such effects the highest interest has been currently aroused by the impurity segregation in the alloys under highly energetic exposure [5].

Vacancy creation energy theoretical calculation techniques exist nowadays. Using these techniques it becomes possible to choose the necessary modes for creating directed vacancy flow. One of such techniques is depicted in [6].

The difference in damageability by various radiation types is related to their penetrability and defect collection kinetics. While analyzing the defect appearance it is necessary to take into account the impact type. Lattice structure defect appearance occurs in the case when the energy transmitted from the ion to the material atoms exceeds the binding energy of the atom in the lattice. The process of defect creation under bombarding particles depends on electron structure of target material. In the case of metals the only process that leads to defect creation is direct elastic energy transmission to material atoms of the target.

The number of displaced atoms in a unit of volume (cm^3) under the absence of displacement cascade can be defined using a formula:

$$n_1 = FNS_k(E_i)\frac{E_{tr}}{E_{thr}} \qquad (2)$$

where: $S_k(E_i)$ — stopping ability of the kernels, eV·cm^2;
N — target atom density, cm^{-3};
F — ion impact doze, ion/cm^2;
E_{tr} — energy transmitted in the atomic collision, eV

$$E_{tr} = \frac{4E_iM_1M_2}{(M_1+M_2)^2} \qquad (3)$$

E_i — ion energy, eV;
E_{thr} — threshold energy of sputtering

$$E_{thr} = \frac{(M_1+M_2)^2}{M_1M_2}E_{sub} \qquad (4)$$

E_{sub} — material sublimation energy, eV.

S_k is calculated as follows:

$$S_k = 2{,}8\cdot10^{-15}\frac{Z_1Z_2}{(Z_1+Z_2)^{1/2}}\frac{M_1}{(M_1+M_2)} \qquad (5)$$

where: M_1 — bombarding particle mass, kg;

M_2 — target atom mass, kg;
Z_1 — bombarding particle charge, Cl;
Z_2 — target atom ctarge, Cl.

In the case when the cascade of displaced atoms appears the equation for their calculation is complicated. Each collision act between ion and atom as well as ion and ion is calculated. There exists a simplified formula

$$n_i = (0{,}56 + 0{,}56\frac{E_i}{E_{thr}})n_1 \tag{6}$$

where: n_i — number of displaced atoms under cascade of displacements, cm^{-3}.

Thus, experimental data usually sufficiently differs from theoretical due to neglecting a number of factors [6].

Having theoretical calculations using such technique it is possible to choose modes for carrying out ion--plasma processing aimed at getting the effect of ascending diffusion in titanium-aluminium alloy.

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