Ti – based biomaterials -properties and production

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The development of new biomaterials is one of the most challenging tasks in the material science. They can improve the quality and length of human life. Biomaterials should have such properties that ensure implants and devices durability and thus completely avoid reoperation or increased service period. Titanium (Ti) is a suitable biomaterial because it cannot magnetise and has suitable mechanical and surface properties. The characteristics of Ti and of its alloys can be improved selectively by using proper technique of the surface processing which preserves the most useful material characteristics.

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1. Introduction

Biomaterials are either artificial or natural materials for production of implants (structures) which can replace and/or restore the function of the lost, injured or diseased biological structures.

Diverse materials used for production of implants and devices can be classified in the following groups: (1) metals, (2) polymers, (3) ceramics, (4) composites and (5) natural materials [1]. The medical application determines the biomaterial design and type. Development of the new biomaterials is a multidisciplinary problem which supposes the mutual work of the scientists, biomedical engineers, pathologists and physicians [2].

Ti and its alloys are widely used in biomedical devices and components. They are used for reparation and construction of bones, drafting dental implants, reconstruction of blood vessels and of the heart muscle [1, 3]. However, Ti and its alloys cannot meet all clinical requirements. Therefore in order to make better biological, chemical and mechanical characteristics the Ti surface must be modified. Resistance to wear, corrosion resistance, and biological properties of Ti and Ti alloys can be improved selectively by using appropriate surface treatment techniques which retain the most useful characteristics of the material [3].

2. Essential properties of biomaterials for making bio-implants and bio-devices

Ti alloys, due to their excellent mechanical, physical and biological performances, are finding ever-increasing application in biomedical devices [4].

Proper material design of implants should to provide their durability, functionality and compatible biological response. Durability and functionality are regulated by the material characteristics.

Following the application requirements and normal functioning of patients, the material for implants may fail due to its plastic defformation, fatigue, expansion, corrossion, wear, and impact fracture. Because the atoms at the implant surface are included in the biological reactions tissue-surface of implants, the characterization and estimation of the surface characteristics are very significant in determining the biocompatibility with the environment [1].

The various phenomena may occur at the interface implant – tissue after implantation of a biomaterial into a living system (Fig. 1). Initially the proteins respond to the implant surface and form a thin layer on the surface within a few seconds. Since cells respond to the proteins, this protein layer then controls the subsequent bioreaction. The cells then multiply and organize into various types of complex tissues. Therefore, the adsorption of proteins plays a vital role in determining the nature of the tissue–implant interface. Protein adsorption to the surface of a biomaterial depends both on the type of protein and nature of the surface [1].

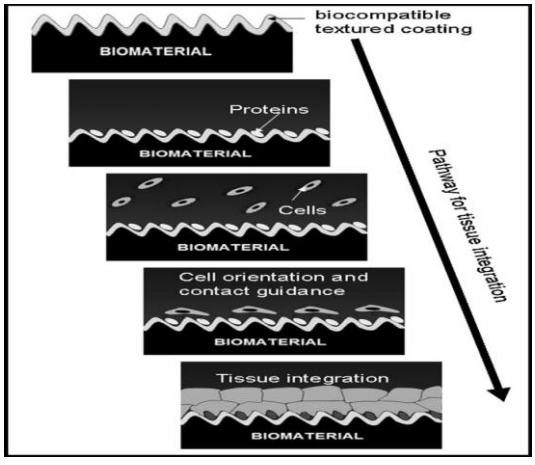

Fig. 1. Schematic illustration of the sequential reactions that take place after the implantation of a biomaterial into a living system [1].

3. Mechanical characteristics

Mechanical characteristics of the materials determine their suitability for certain application.

For all implants it is necessary to use materials with excellent combination of high strength and low modulus of elasticity, which approximates the elastic modulus of the bone to avoid loosening of the implant which prevents new surgery interventions and ensures the longer period maintenance [1, 2].

In order to develop a durable device, testing the resistance to fatigue it is crucial for predicting the durability of implants [5, 6]. Material fatigue is determined by the stability of the material under the cyclic application of the load. In the presence of cyclic load, the material can be damaged by stress, whose value is less than the stress causing tearing of the material. In the design of metal implants, to be used in the body, it is important to ensure that the level of stress is found below a certain threshold which is called the fatigue endurance limit, in order to avoid failures [7].

4. Resistance to corrosion and wear

All metals and alloys are exposed to corrosion during the contact with the body liquids as is the living environment which is agressive due to the presence, for example, the Cl ions and proteins [2]. Low resistance to wear and corrosion of implants in human body's liquids results into the release of non compatible metal ions in the body. It is found that they can cause the allergic and toxic reactions [8]. The maintenance period of the materials is mainly determined by their resistance to wear. Low resistance causes the losses in implants and some reactions in tissues [9]. Therefore the development of implants with high resistance to corrosion and wear is of primary importance for the longevity of the material in the human body.

5. Surface properties

The biomaterials in clinical practice should not to be toxic, carciogenic, immunogenic, allergenic, magnetic and radioactive. They have to be biotolerant. Biotolerance means the compatibility with the living organism. Biocompatibility proposes, in general, the absence of any immunological response of the organism and presents very important property in clinic practice.

In the living tissue, the implant surfaces react immediately, so that new connections and compounds are formed from thermodynamical and kinetical reasons that minimize the surface energy. Biomaterial surface possesses diverse morphologies and chemical content which can strongly affect interactions between the implants, and cells and thus, the integration of tissue into the damaged areas [1].

Morphological characteristics as the surface roughness and topology, strongly affect the protein adsorption, attachment, proliferation of cells and their differentiation [10-12].

Chemical composition of surface determines the type of the intermolecular forces and interactions with the proteins.

The surface potential affects the structure and chemical composition of the biomaterial environment. It also affects the distribution of the ions in solution and, in this way, their interactions with proteins [1].

6. Characteristics of the Ti alloys and Ti

Ti alloys are expected to be much more widely used for implant materials in the medical and dental fields because of their superior biocompatibility, corrosion resistance and specific strength compared with other metallic implant materials [13]. Ti readily adsorbs proteins from biological fluids. The surfaces of Ti can also support cell growth and differentiation [3]. The Ti surface reacts with oxygen forming a layer of titanium oxide (TiO_2) that significantly reduces, but is not able to completely avoid, the ion release. The biocompatibility of Ti is mostly attributed to its oxide layer [14]. This protective layer decreases the metal reactivity [15]. This layer can be spontaneously restored after being damaged, even in the solutions with low content of oxygen [16]. A thin, dense protective oxide layer (mainly TiO_2) is formed rapidly in the Ti surface when exposed to air [17]. Properties of the TiO_2 layer at the surfaces of implants are determinant for a good contact with the tissue. Oxide characteristics may be deliberately changed [18].

The coating layer prepared by nanometer TiO_2 powders using the process that Ti alloys were embedded into nanometer TiO_2 powders and sintered in a high temperature furnace, possesses an excellent biocompatibility [19]. Formation of TiO_2 nano-network on Ti surface increases the human cell growth using a simple electrochemical anodization treatment [17]. TiO_2 particles are frequently used as a white pigment colour and as components of the cosmetic products [20]. The rational combination of cinnamates and TiO_2 has shown a synergic effect to improve the sun protection factor (SPF) of cosmetic preparations [21]. In the absence of UV radiation or visible light *in vitro* TiO_2 particles are not at all genotoxic or are weakly genotoxic. But being irradiated TiO_2 particles exhibited significant genotoxicity in the single cell gel and chromosomal aberration assays [20]. Studies of acute oral toxicity in rats, dermal irritation studies in rabbits and skin sensitization assays in mice demonstrated that ultrafine TiO_2 particles had low oral toxicity, and was not able to cause skin irritation or dermal sensitization. Exposures to ultrafine TiO_2 particles can produce differential pulmonary effects, based upon their composition, and crystal structure. Inhaled rutile ultrafine TiO_2 particles are expected to have a low risk potential for producing adverse pulmonary health effects [22, 23]. Li *et al*. fabricated the one-dimensional TiO_2 whiskers (TiO_2 Ws) and designed a strategy to explore their drug delivery application and anti-tumour function combined with

daunorubicin (DNR). In human hepatocarcinoma cells (SMMC-7721 cells), TiO_2 Ws can obviously increase the intracellular concentration of DNR and enhance its potential anti-tumour efficiency, indicating that TiO_2 Ws could produce an efficient drug delivery effect importing DNR into target cells. Furthermore, its photocatalysis further led to the enhanced mortality of cancer cells under UV irradiation [24].

Although there are many forms of corrosion damage, the extent of general corrosion attack on the majority of metal implants, that are currently used, is very weak due to the presence of passive layer on the surface [2,25]. Ti has the highest resistance to general corrosion, pitting corrosion, and corrosion cracking in comparison with other metals or alloys such as stainless steel and chromium cobalt [15, 26].

Implant pitting corrosion (Fig. 2) is dominant in the oral cavity due to the increased availability of oxygen and acid foods in the environment [2]. In the oral cavity, organic acids as the lactic acid and formic acid make plaque on teeth. Type and concentration of the organic acids can vary depending on the type of environment: aneorobic or aerobic. The corrosive properties of Ti are markedly dependent on pH in formic acid, and relatively less dependent on pH in lactic acid in which Ti is dissolvable at pH 1.0-8.5 [27]. Patients with dental prostheses or implants made of pure Ti or Ti alloys to Fe should not to use fluoride gels for dental protection, because fluoride ions can damage the protective passivation layer which usually exists on Ti and its alloys, which leads to pitting corrosion [28].

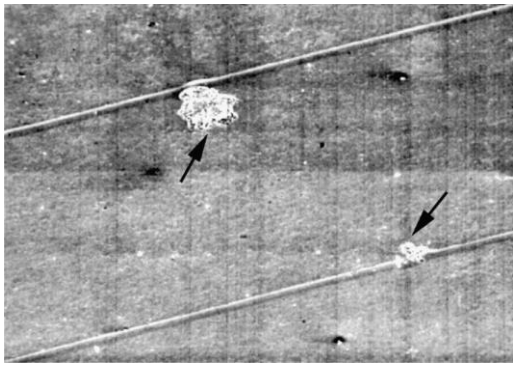

Fig. 2. Experimental titanium implant (pitting corrosion). Scanning electron microscopy image showing pits (arrowed) along the surface cracks. ×85 [15].

Pure Ti and Ti–6Al–4V (Titanium-Aluminium-Vanadium) alloy, in particular, Ti–6Al–4V ELI (Ti64, Extra Low interstitial) have been mainly used as implant materials [3, 25, 29]. However, there is a great concern on the dissolution of Al and V ions into the body fluid and the possibility of causing toxic effect, as a result of the breaking of the surface layer of alloy Ti–6Al–4V [29, 30]. Al- and V-free Ti alloys as implant materials have been developed because toxicity of V and Al has been pointed [29]. The tensile strength and elongation of Ti–29Nb–13Ta–4.6Zr (Titanium-Niobium-Talium-Zirconium) alloy is equivalent to or greater than those of conventional Ti alloys for implant materials. The moduli of elasticity of the designed alloys are lower compared with those of conventional biomedical Ti alloys such as Ti-6Al-4V ELI [29, 31].

Porosive Ti is very popular in surgery for implants. Its low elasticity module stimulates the bones growth. The bad characteristics are the instability to friction and wear. By addition of C, the friction coefficient become smaller and Ti carbide increases the resistivity to the wear, so that it is possible to produce multicomponent material that overcomes these drawbacks. On the other hand, C can increase the corrosivity rate of Ti. Therefore, depending on the specific requirements for the implant, C may be added to the extent that would be a compromise between improved anti-friction characteristics and of the lack of increased corrosion [32].

Titanium–nickel (NiTi, Nitinol) alloy found many applications in industry and medicine [3, 33, 34]. The memory shape NiTi alloys is composed of 55% Ni and 45% Ti, and is often referred to as Nitinol (Ni-nickel, Ti - titanium, word NOL was added due to the name of laboratories-Naval Ordinance Laboratory, where Buehler and his colleagues discovered mentioned alloys) [3]. Nitinol is one of the most promising Ti implants that has a large number of different applications. The reason is that Nitinol is characterized by suitable shape memory effect, improved biocompatibility and superelasticity [3, 33, 34].

7. Production of the biomaterials based on Ti

For highly specialized applications, Ti ingots are made of titanium sponge. As biomaterials Ti ingots can be carried out by vacuum induction furnace or magnetic suspension vacuum furnace by melting and casting. Ti alloy ingots were shaped into many specimens with any shape and size [35].

The production by powder metallurgy parts is making use of the powders instead of sponge titanium. The powders can be directly rolled into any shape or final products. The powder production process is very expensive. Thus the finding of the new production processes for obtaining the Ti powder directly from Ti ore that will lead to much cheaper titanium powder is a challenge [35]. A few procedures for processing powder into components exist: molding of the injected metal powders (MIM) developed on powder binding by adhesives and removing of the agglomerates by heating; junction of powder by direct powder rolling (DPR) into sheet of powdered components, and then heating and sintering; hot isostatic pressing (HIP)-casting in which the powder is heated under the high pressure forming certain form by casting [35].

Electric Current Activated/assisted Sintering technique (ECAS) – i.e. sintering by the electrical current, is a technique for obtaining dense materials including the nanostructured ones. It has technological and economic advances over the conventional sintering methods as are

larger heating rate, lower sintering temperature, lower retention time, absence of the cold compression, lower sensitivity to initial powder charactreristics and significant improvements in material qualities [36]. Porosive compact Ti is effectively produced by the sintering process in the presence of electrical discharge (EDS) for the time interval shorter than 400 μs [37-40].

Standard production processes for obtaining the Ti implants usually cause oxidation, contamination of the surface layer which are often strained and plastically deformed, non-uniform and weakly defined. Such 'native' surfaces do not suit for biomedical applications without some additional surface processing. Proper techniques for surface modification not only preserves the good properties of Ti and its alloys, as relatively low elasticity module, good fatigue of the material, but also make better specific surface properties neccessary for clinical practice [3].

Surface modifications can be selected in two categories: (1) chemical or physical changes of the atoms, compounds or molecules on the surface (erosion and chemical changes) and (2) surface coating with materials of different structures [41]. Technologies for modification of surfaces are clasified as mechanical, chemical, and physical according to the mechanism of the surface layer formation [3].

Ti can form apatite layer which looks like bone at the Ti surface in the simulating body liquid (SBF) when the surface is treated by NaOH. Ti with the lowest content of Na^+ may be suitable for use in the human body, because the amount of alkali ions released into the surrounding tissue is small, and the degree of apatite formation is the same as for the Ti with the highest content of Na^+ in the surface layer [42].

It is found that alkaline and thermally processed porosive Ti possesses good mechanical properties and biocompatibility for clinical practice [43]. Alkali-heat treatment significantly increased the surface energy of Ti samples as compared to untreated samples [44]. It is found *in vitro* that the Ti without Na with specific structure of anatase and rutile possesses higher ability to form apatite than Ti with Na. Therefore it is possible to form several bioactive Ti alloys by transforming sodium titanate surface into titania without sodium. This can be done by elimination of sodium by a combined treatment with NaOH and heat treatment, or by forming titania through different methodology [45, 46].

Anode oxidation is a method developed for production of different types of the protecting oxide layers on metal. Different diluted acids (H_2SO_4, H_3PO_4, CH_3COOH, etc.) can be applied as electrolites in the mentioned process. After anodic oxidation in H_2SO_4 [46, 47] and Na_2SO_4 [47] solutions, porous titania layers mainly consisted of rutile or rutile/anatase phases produced on the surface of Ti, which could effectively induce apatite formation in a short time in SBF. However, amorphous titania layers on Ti metal subjected to anodizing in CH_3COOH and H_3PO_4 solutions could not induce apatite formation in SBF [47]. The rutile structure of titania played an important role in inducing the apatite deposition because of the relationship of lattice matching between rutile and apatite [46, 47]. If the electrolite is NaCl, Ti plates anodized in NaCl demonstrate much greater antibacterial activity, and antibacterial titanium is a promising material for use in dental implant systems [48]. In the electrolyte of calcium glycerophosphate and calcium acetate, the anodic TiO_2 is porous, highly crystalline, and rich in Ca and P. All the surface properties of the anodic oxide have the promising positive biological response [49].

If the anodic process is performed at voltage above the breakdown limit, oxide will not be enough resistant to prevent the further flow of current. At such high voltage, the process will lead to increased formation of gas and frequent sparking. This type of anodization is known as anodization by sparking, which usually leads to less uniform and porosity of oxide layers. Anode sparking in oxidation process often is recognized as a micro-arc oxidation (MAO) or plasma electrolitic oxidation [3]. MAO can be used for coating of implants, because it results into the porosive, rough and solid adhesive ceramical layers on the metal surfaces. The porous nature of the ceramic coating can cause an increase possibilities the implants to generate new bone tissue, and may open the way for installation of the implants antibiotics and antibiotic release [50,51] around the implant [1]. Quality of the MAO layer is determined by the combination of properly selected parameters as composition of electrolites [52], their temperature, alloys composition, voltage, current density, time, etc. [3]. The electrolitic deposition is widely used for sinthesies of the Ca P coating on different materials for implants due to the simplicity of the process, low price of the equipment, ability to form layers on the samples of complex shape [1,53].

Plasma-surface modification is of growing interest in biomedical engineering. Plasma is very reactive medium which nicely interact with surfaces. Thus, it was found application in preparation of the biomedical coating on implants of Ti in orthopedy [41]. This technique is the most effective and very economical for formation of the hydroxyapatite layers [54]. Ti oxide and Ti nitride layers coated onto Ti alloys by plasma oxidation and nitration, by applying the glow discharge treatment, essentially improve the properties of the Ti alloys, as well as their biocompatibility in *in vitro* tests [55].

8. Conclusion

Ti and its alloys are not ideal biomaterials. However, they satisfy the fundamental request for implants – biocompatibility - i.e. do not cause immune response of the living organism. By proper selection of the elements which to be added to Ti, of techniques for obtaining alloys, and the surface modifications, it is possible to create biomaterials on the Ti base with suitable characteristics for certain medical application.

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