

Nanometals for next-generation medical implants**Нанометаллы для медицинских имплантатов нового поколения***R. Z. Valiev* *, *E. D. Khafizova**P. Z. Valiev* *, *Э. Д. Хафизова*

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ABSTRACT

Today, the development and manufacture of medical implants and products is an actively progressing scientific and technical area that includes the development of new materials and design technologies, the manufacture of new products, quality control and the training of engineering and medical professionals. The reports presented in this session will introduce the audience to new developments in the area of nanostructured metallic biomaterials for dentistry and surgery. Nanostructured metallic materials have enhanced strength and lifetime. Surface modification by means of chemical etching and the deposition of bioactive coatings significantly increases the biomedical properties of a material. Nanomaterials provide an opportunity to design and create new medical implants with an improved design and an enhanced functionality for dentistry and surgery. The emergence of additive technologies enables the manufacture of medical products for various purposes or in different sizes, and reducing the product mass and the time of prototype manufacture, and most importantly – allows custom sizes.

KEYWORDS

Medical implants; nanometals; enhanced strength; enhanced biomedical properties.

АННОТАЦИЯ

На сегодняшний день разработка и производство медицинских имплантатов и изделий – это интенсивно развивающееся научно-техническое направление, которое включает в себя разработку новых материалов, технологий проектирования, производство новых изделий, контроль качества и подготовку технических и медицинских кадров. Доклады данной секции знакомят с новыми разработками наноструктурных металлических биоматериалов в стоматологии и хирургии. Наноструктурные металлические материалы отличаются повышенной прочностью и долговечностью. Модификации поверхности с помощью химического травления, нанесения биоактивных покрытий значительно повышают биомедицинские свойства материала. Наноматериалы дают возможность проектировать и создавать новые медицинские имплантаты улучшенной конструкции и повышенной функциональности в стоматологии и хирургии. Появление аддитивных технологий дает возможность изготовления медицинских изделий различного назначения или размера, снижать массу изделий и сроки производства прототипов, а главное индивидуальных размеров.

КЛЮЧЕВЫЕ СЛОВА

Медицинские имплантаты; нанометаллы; повышенная прочность; повышенные биомедицинские свойства.

Introduction

At present, the research area of biomaterials is among the major ones in today's materials science and forms the foundation for the design of new medical products. Research and development is under way on the design of high-strength biomaterials for implants, both bioinert [1] and biodegradable [2], biomimetic coatings

for implants [3], hybrid organic materials for the modeling of the biocompatibility of medical implants [4], the application of additive technologies in surgical practice, medical exoskeletons [5], etc.

New alloys with optimized chemical compositions, fabrication methods, and improved surfaces are the object of continuous research

and development aimed at satisfying the clinical demand for medical devices. Currently, the main metallic materials for medical implants are stainless steels, Co and Ti alloys, commercially pure (CP) Ti. Recently, a great interest was aroused by biodegradable materials, in particular, Mg alloys, for implants, stents and other medical products [2]. Today, over 70% of implants are produced from metallic materials. A medical material must be biofunctional and safe since there is a danger of the toxic action of metal ions on human body.

In today's materials science, a promising area is the improvement of the strength properties and other mechanical functional properties of metals and alloys by means of their nanostructuring via severe plastic deformation (SPD) processing based on the use of large plastic strains under the conditions of elevated pressures and relatively low homologous temperatures [6]. This type of processing приводит leads to the nanostructuring of materials where the grain structure is refined to the submicron or nanometric diameters, and there may form clusters and nanoprecipitates of secondary phases that have a great effect on the mechanical and functional properties of metallic materials [6].

The use of SPD processing in designing nanomaterials for medical applications is a breakthrough area for creating next-generation implants and items. This paper presents in brief the results of recent research in this area of high current importance.

1. Medical metallic materials

Traditionally, many medical materials are stainless steels that have a good corrosion resistance, strength and ductility, and most importantly, are relatively cheap. There are many studies dealing with the problem of strengthening of stainless steels by SPD processing.

For example, for the stainless steel 316L SPD processing increased strength by a factor of 3, from 515 MPa to 1647 MPa [7]. According to [8], for the nanostructured steel 316L the highest yield strength value of 2230 MPa was obtained.

Severe plastic deformation results in strong changes in the material's microstructure and phase composition that require comprehensive investigations and experiments. Under this type of deformation, there occur unusual, in comparison to conventional treatments, phase transformations. For example, strain-induced martensite was observed after SPD processing in the stainless steels 301 [9] and 304 [10]. After severe deformations, materials contain in their interiors fine grains with different nanostructural elements, such as nanotwins, microslip bands, very high dislocation densities and a substructure. Nanostructural elements may have a great effect on the behavior of metals during annealing and recrystallization, and on their mechanical properties. Stainless steels [11] processed by SPD exhibit an enhanced corrosion resistance and provide an intensive cell growth and multiplication [12]. These results enable predicting a high potential of nanostructured stainless steels for biomedical applications.

At the same time, iron has a negative reaction to modern diagnostic apparatuses such as computer tomographs (CT), magnetic resonance imaging (MRI) scanners.

Solving this problem involves the use of titanium and Ti-based alloys, although they are much more expensive than stainless steels. Ti is more practical and is not affected by corrosion, it is more biologically neutral. The corrosion resistance of Ti is due to the fact that at temperatures up to 530–560 °C this metal's surface is covered by an extremely strong natural protective film of TiO₂ ensuring the formation of a stable surface onto which a mineralized bone matrix may be mounted. This film has a thickness of 50–100 Å and is biologically harmless, therefore it prevents any reaction between the metal and a human body [13].

Today, medicine uses a large range of Ti alloys with different chemical compositions and mechanotechnological parameters. The most often used alloying additions are Ta, Al, V, Mo, Mg, Cr, Si, and Sn. Dentistry and orthopedics tend to use more the alloys Ti-6Al-4V(Ti64) and Ti-6Al-7Nb [14]. However, Al and especially

V are rather toxic elements, while CP Grade 4 Ti has the best biocompatibility with living tissues [13]. However, this material has low strength properties that have been considerably enhanced by severe deformation. Using SPD processing, nanostructured CP Ti was produced with mechanical properties increased to 1240 MPa, the ultimate tensile strength (UTS) of the initial CP Ti being 700 MPa [15], and an improved biological response of the titanium's surface [15, 16]. The strength of CP Ti in the nanostructured state is more than twice higher than that of the initial material, without any considerable decline in ductility.

Nanostructured CP Ti is produced in the form of rods by SPD, specifically by equal-channel angular pressing (ECAP) followed by heat treatment [17] and by ECAP-Conform [15] followed by drawing to achieve the required length and a homogeneous structure across the whole length of the three-meter rod. After this type of treatment, nanostructured CP Ti has a strength and fatigue life twice or more higher than conventional CP Ti and even the Ti-6Al-4V alloy [13]. The high strength of nanotitanium makes it possible to use implants of a smaller size, which reduces surgical intervention. The presence of grains with a size up to 150 nm and non-equilibrium deformation-distorted grain boundaries in SPD-processed nanotitanium considerably increases the material's internal energy [17], which changes the oxide film's morphology and provides the best acceptance of Ti by cells [14].

2. Biodegradable metallic materials

A research area of high current importance is the development of new biodegradable materials that are fully dissolved in a human body in a certain period of time. To date, there have been comprehensive studies of Mg and its alloys [18], Fe [19]; recently, a great interest was aroused by Zn and its alloys due to zinc's perfect rate of dissolution in a human body [20].

The strength of Zn alloys is lower than that of Fe-based biomedical alloys, but higher than that of Mg alloys; the solubility of Zn alloys is lower

than that of bioresorbable Mg alloys, but higher than that of Fe-based alloys. In [21–23], several alloys were investigated for application in next-generation biodegradable bone implants based on Zn. It was found that Zn-Li alloys [22] are the most promising ones for biomedical applications. Preliminary in vitro and in vivo studies showed that, unlike Fe- and Mg-based materials, Zn-based materials degrade with a perfect rate and have a satisfactory biocompatibility.

Most commercial Zn alloys are alloys based on ZnAl, and according to ASTM B86-18 their UTS and ductility are 283–359 MPa and 7–13%, respectively [23], while Zn-Li alloys (Zn-0.4 wt.% Li) exhibit higher UTS and ductility values of 520 MPa and 5%, respectively [2].

The nanostructuring of biodegradable alloys for application in stents and plates is a task of high current importance, but for each specific alloys the processing should be carefully defined, which makes solving this problem attractive for further research [24].

Conclusions

The recent research results presented in this overview demonstrate that metallic biomaterials after their nanostructuring exhibit significantly improved mechanical and functional properties. Such properties open up new opportunities for the manufacture of next-generation implants with an improved design and enhanced functionality.

Acknowledgements

This research was supported by the Russian Science Foundation under project no. 20-63-47027.

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