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Modification of Ti6Al4V surface by diazonium compounds

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ABSTRACT

Ti6Al4V alloy is the most commonly used in orthopedic industry as an endoprosthesis. Ti6Al4V exhibits good mechanical properties, except the abrasion resistance. Surface modification of Ti6Al4V in order to obtain organic layer, and then the attachment of the polymer, can allow for overcoming this problem. The aim of the work was the modification of Ti6Al4V surface by diazonium compounds: salt or cation generated in situ and examine the influence of the reducing agent - ascorbic acid, and the temperature of reaction on modification process. Moreover, the simulated body fluid was used for the assessment of the organic layer stability on Ti6Al4V surface. The evaluation of the modification was carried out using the following methods: Raman microspectroscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy. Higher temperature of modification by 4-hydroxymethylbenzenediazonium cation, provides the largest amount of organic layer on the Ti6Al4V alloy. In the case of the Ti6Al4V modified by Variamine Blue B salt, the amount of organic layer is not dependent on the reaction condition. Moreover, the ascorbic acid and the presence of TiO_2 does not effect on the modification. The modified surface is completely coated with the organic layer which is stable in simulated body fluid.

1. Introduction

Titanium alloys are widely used in the orthopedic and dental implants, chemical process industry, automotive and aerospace structural parts [1]. They are known as the most suitable materials for biomedical applications because of their excellent biocompatibility, corrosion resistance and low elastic modulus comparable with that of human bone [2]. Despite its many advantages, the titanium alloys have poor abrasion resistance. Therefore, the use of the titanium in friction parts is limited. Surface treatment of titanium alloys improves the wear resistance, however, it often involves a deterioration of fatigue strength [3]. The literature describes many examples of the surface modification of titanium alloys such as physical deposition methods (ion implantation and plasma spray coating), thermo-chemical surface treatments (nitriding, carburization and boriding) [4]. Despite so many methods of modification of titanium alloys, they still have not a suitable abrasion resistance. Ti6Al4V alloy, which has been modified in this research, is the most commonly and widely used in orthopedic industry as an endoprosthesis. Biocompatibility of Ti6Al4V alloy is satisfactory, especially when direct contact with tissue or bone is required [5]. Moreover, Ti6Al4V alloy exhibits good mechanical properties, except the abrasion resistance. Poor surface wear properties of Ti6Al4V alloy is associated with the release of vanadium and aluminum ions. Both ions are associated with long-term health problems, such as Alzheimer disease and neuropathy [6]. Surface modification of Ti6Al4V alloy in order to obtain organic layer, and then the attachment of the polymer, can allow for overcoming this problem.

The surface and interface chemistry of aryl diazonium salts is well known [7,8]. The diazonium salts are used to modify and change the physicochemical properties of a broad range of materials such as carbon, metals, metal oxides and ceramics relevant to many fields of life (medicine, electronics, environment, etc.) [9–15]. The diazonium salts have been used in the modification of the materials surface in order to obtain the aryl layer which may react with the monomers to form a polymer layer. The surface of graphene was modified by diazonium salt with alcohol groups which are then reacted with isocyanate-terminated polyurethane and a polymer layer on the surface of graphene was obtained [16]. The surface of titanium compounds was earlier modified by using the diazonium salt. Mesnage et al. described grafting process based on the chemical reduction of diazonium salt by reducing agents (ascorbic acid) in presence of the vinylic monomer in order to obtain on the surface of titanium oxide the poly(hydroxyethyl) methacrylate [17]. Elsewhere, Zeb with collaborators obtained polyaminophenyl layer on the surface of titanium nitride what can serve for subsequent electroless deposition of various metals (nickel, copper) [18]. Despite reports describing a modification of titanium compounds by diazonium salts, there are no reports on the modification of titanium alloys.

The aim of the work was the modification of Ti6Al4V alloy surface (with and without oxide layer) by diazonium compounds: salt or cation

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Table 1
The chemical composition of Ti6Al4V alloy used in this study (mass %).

Al	V	C	Fe	O	N	H	Ti
6.0	4.0	0.03	0.1	0.1	0.01	0.003	Bal.

Table 2
Reagents, their purities and amounts for preparing 1000 mL of the SBFs.

Reagents	Purity/%	Amount
NaCl	>99.0	8.036 g
$NaHCO_3$	>99.0	0.352 g
KCl	>98.0	0.225 g
$K_2HPO_4 * 3H_2O$	>99.0	0.230 g
$MgCl_2 * 6H_2O$	>99.0	0.311 g
1.0 M–HCl	–	40 mL
$CaCl_2$	>96.0	0.293 g
Na_2SO_4	>99.0	0.072 g
TRIS	>99.8	6.063 g
1.0 M–HCl	–	0.2 mL

generated in situ and examine the influence of the reducing agent (ascorbic acid) and the higher temperature of reaction (50 °C) on modification process. In this work, we could not apply other reducing agents such as phosphorous acid due to the fact that the acid would react with the alloy surface. Moreover, the electrochemical reduction could not be applied to this type of grain. Furthermore, the simulated body fluid (SBF) with ion concentrations approximately equal to those of human blood plasma was used for the assessment of the organic layer stability on Ti6Al4V alloy surface [19,20]. In the near future, the next polymer layer will be formed on the organic layer. However, this step of modification is not presented in this article. The evaluation of Ti6Al4V alloy modification was carried out using the following methods: Raman microspectroscopy (Raman scattering and fluorescence intensity), scanning electron microscopy and energy-dispersive X-ray spectroscopy.

2. Materials and Methods

2.1. Materials

Titanium alloy - Ti6Al4V (Table 1) was supplied by Arcam AB, Sweden (powder between 45 and 100 μm). Other chemical reagents i.e. Variamine Blue B salt - VB (4-amino-4′-methoxydiphenylamine-diazonium chloride), 4-aminobenzyl alcohol (98%), sodium nitrite (99.5%), potassium phosphate dibasic trihydrate (99%), sodium bicarbonate (99%), magnesium chloride hexahydrate (99%) potassium phosphate monobasic (99%), sodium sulphate (99%) calcium chloride (96%) and tris(hydroxymethyl)aminomethane (99.8%) (TRIS) were obtained from Sigma-Aldrich. Potassium chloride of high purity was supplied by Chempur (Poland). Hydrochloric acid (36–38%) and sodium chloride (99%) were obtained from POCh (Gliwice, Poland).

2.2. Preparation of Titanium Oxide on the Alloy Surface

The Ti6Al4V alloy has been annealed in a furnace at 100 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C for 15 h.

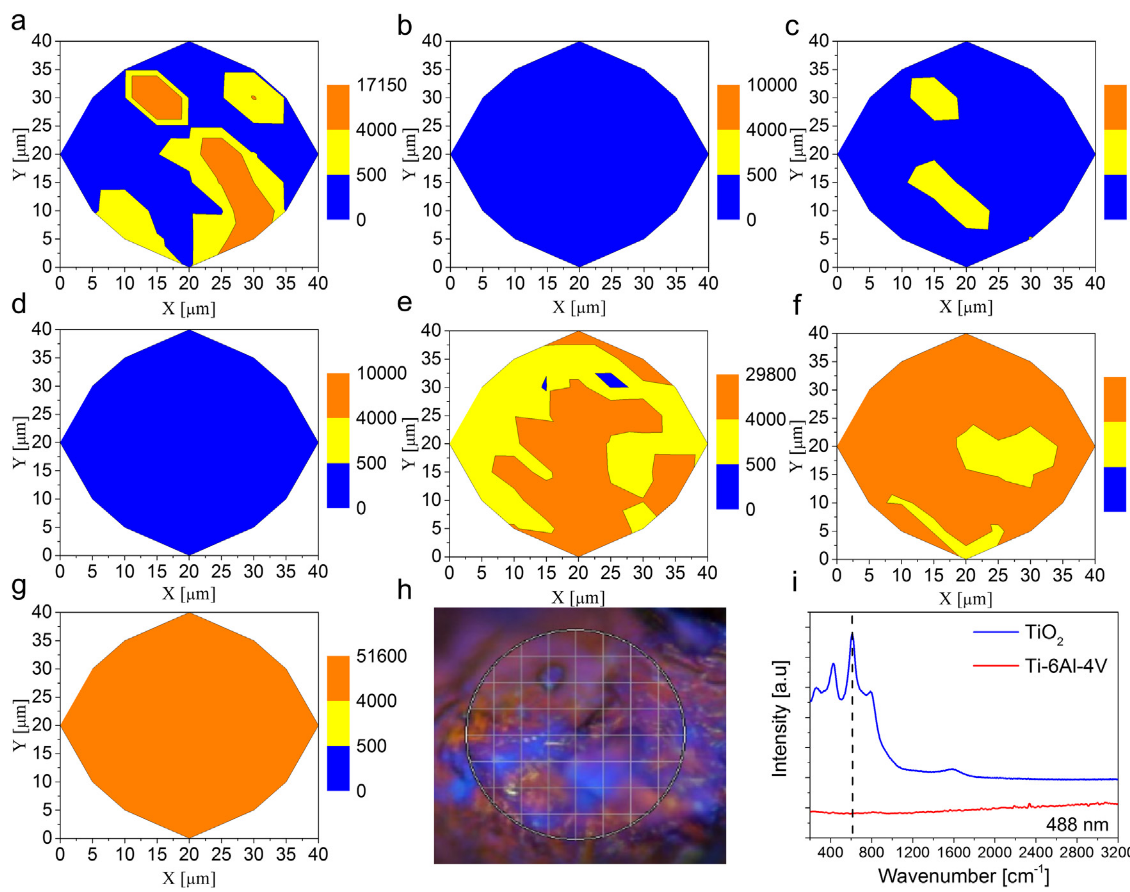

Fig. 1. The images based on the signal intensity at 608 cm^{-1} recorded on the single grain of unheated (a), and annealed at 100 °C (b), 200 °C (c), 300 °C (d), 400 °C (e), 500 °C (f), 600 °C (g) Ti6Al4V alloy. The photo (h) with a grid of Raman spectra measurements on Ti6Al4V alloy. Raman spectra of the unheated Ti6Al4V alloy and TiO_2 locating on the surface of annealed Ti6Al4V alloy (i).