STRUCTURE AND PROPERTIES OF THE MULTICOMONENT SURFACE LAYERS PRODUCED BY COMBINED METHODS UNDER GLOW DISCHARGE CONDITIONS.

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Abstract

The paper presents the results of examinations of the metallurgical surface topography, the phase and chemical compositions, the corrosion and wear resistance of the (Ti,Ni)3P + Ti5P + (Ni,Ti) type multicomponent surface layers produced on titanium alloy Ti-1Al-1Mn type by a chemical nickel electroless deposition process combined with a glow discharge assisted treatment, the biocompatibility of these layers was examined by in vitro test. The results show, that the multicomponent surface layers have good corrosion and wear resistance properties and a good biocompatibility.

1. Introduction

The requirements for modern materials of high performance properties have prompted the development of various material treatment techniques and their combinations. Such combined methods facilitate controlling the chemical and phase composition, microstructure, surface topography of the layer’s thus produced, thereby controlling their performance properties and, on the other hand, improving their adhesion to the substrate due to the diffusion involved in these processes.[1-5] It is also expected that the surface layers can protect the alloys against ion release from which is strongly related to the biocompatibility. Even in the titanium alloys showing a very high biocompatibility ion release occur e.g. nickel from the titanium – nickel (memory shape) alloy. Nickel ions may promote toxic, allergic and inflammatory processes [6,7]. An effective method of preventing this ion release consists of subjecting the titanium alloys to surface treatments. The surface engineering techniques used for this purpose include thermal spraying, ion implantation and glow discharge assisted treatments [8-10].

The aim of this study was to produce composite layers on a titanium alloy, which improve its biocompatibility by preventing the Ni and Ti release.

This paper presents a new composite and multicomponent layer – of the (Ti,Ni)3P + Ti5P + (Ni,Ti) type, produced on titanium alloys by the electroless nickel deposition method combined with a plasma treatment under glow discharge conditions.

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2. Experimental procedure

Specimens of the Ti-1Al-1Mn titanium alloy were subjected to nickel electroless chemical deposition in a water solution containing: NiCl₂, NaHPO₄ and CH₃COONa at a temperature of 95°C for 1h. The 4μm thick Ni coatings thus produced, containing 16% of phosphorus, were subjected to a glow discharge treatment in an argon atmosphere at a temperature of 700°C.

The surface layers obtained were examined regards:

- Vickers microhardness using a Neophot microscope equipped with a Hanemann unit,
- metallographic cross – sections prepared using a mixture of: 96 ml H₂O + 2 ml HNO₃ + 2 ml HF,
- surface topography in a Taylor Hobson Form Talysurf Series 2 scanning profilometre,
- chemical composition by GDOS using a Jeol 505 type microanlyser, resolution - 20nm, voltage - 0,7kV, current - 30mA and a Cameca Semprobe SU – 30 X- ray mroanalyser,
- corrosion resistance by the potentiodynamic method in a 0.5 M NaCl solution. The potentiodynamic curves were determined at a temperature of 25°C using an Atlas Sollich potentiostat. The polarization curves were determined by polarizing the samples (starting from a potential of -100mV upwards) at a potential variation rate of 50mV/min. The reference electrode was a saturated calomel electrode (SCE),
- resistance to frictional wear using the three rollers + taper method under a unit load of 100MPa [11]. This test friction is applied among three 8mm diameter cylindrical specimens (rollers) and a rotating conical counterspecimens (taper). The linear wear, expressed as the wear depth, was determined by measuring the diameters of the ellipses formed on the surface layer of the individual rollers. The counterspecimen was made of AISI 45 steel, quench hardened and tempered to hardness of 30HRC. The test time was 100min., but it was interrupted at interval of 10 min. At which time the worn area (elliptical in shape) was measured. After each interruption the load was increased so as to maintain a constant unit load.
- surface topography using a scanning electron microscope Leo 1530,
- biocompatibility in a human fibroblast culture. The cells retrieved from the primary culture were plated on individual samples at a density of 7.5x10⁴ /μl medium and cultured for 12 days. At a term, the cells were detached from the samples by enzymatic dissociation with 0,25% trypsin and a number of the cells were counted in 0,1 ml using a Burcker’s camera. The dead cells in population were recognized by methylene blue staining. Data are presented as means values. Statistical comparisons between the groups were carried out by the variance analysis. In all the comparisons, p<0,05 was considered to be indicative of statistically significant differences. All specimens were exposed to sterilisation procedures by autoclave: steam atmosphere, 30min, 134°C, 1400hPa in one cycle.
- content of metal ions in the cells detached from the sample surfaces and in the incubation medium using a Link System AN 1000 X-ray analyzer.
3. Results

Fig. 1 shows the microstructure and appearance of the surface layers produced on the titanium alloy by chemical electroless nickel deposition combined with a glow discharge enhanced heat treatment in an argon atmosphere.

![Microphotographs](image)

Fig. 1. Microphotographs and appearance of the Ni(P) coatings prior to (a) and after (b) glow discharge enhanced heat treatment in an argon atmosphere

After the glow discharge treatment, the surface microhardness of the Ni(P) layer with a 16% phosphorus content increased from about 700HV0.05 to 1200HV0.05. Table 1 gives the parameters characteristic of the surface topography of the layers, and Fig. 2 shows the distribution of the Ti, Ni, P, Al and Mn concentrations in the composite layer produced during the glow discharge treatment.

Table 1: Stereometric parameters characterizing the topography of the surface of Ni(P) and (Ti,Ni)$_3$P layers.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ni(P)</th>
<th>(Ti,Ni)$_3$P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sa [μm]</td>
<td>0.224</td>
<td>0.172</td>
</tr>
<tr>
<td>Sp [μm]</td>
<td>1.83</td>
<td>1.33</td>
</tr>
<tr>
<td>Sv [μm]</td>
<td>0.935</td>
<td>0.906</td>
</tr>
<tr>
<td>Sq [μm]</td>
<td>0.302</td>
<td>0.228</td>
</tr>
</tbody>
</table>

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Sa – arithmetic mean deviation of the roughness profile; Sp – maximal height of the peak of the roughness profile; Sv – maximal depth of the valley; Sq – square mean deviation of the roughness profile.

Fig. 2. Concentration profiles of Ti, Ni, P, Al and Mn in the surface layer prior to (a) and after the glow discharge treatment of the Ni(P) coatings.

Examinations with an X-ray microanalyser show that the chemical electroless nickel deposition combined with the glow discharge enhanced treatment give composite layers built of several sublayers, such as (beginning from the sample surface downwards): 1 - a (Ti,Ni),P layer, about 2µm thick and composed of Ti-35at.%, Ni-38at.% and P-25at.%, 2 - a 4µm thick Ti,P layer containing ca. 78 %Ti + 22%P, and a diffusion transition zone containing ca. 80%Ti, 11%Ni, 4%Mn and 5%Al. Hence the phase composition of the composite layer being formed is (beginning from the sample surface downwards): (Ti,Ni),P + Ti,P + (Ni,Ti,Mn,Al) diffusion zone. It is worth noting that, by modifying the parameters of the glow discharge enhanced process, we can produce a surface layer that contains the Ti,P phase alone - a phase which was identified [12] e.g. in the transition zone of the hydroxyapatite coating formed on a titanium alloy after it was subjected to heating.

The composite layers have a good corrosion resistance, comparable with that of the Ni(P) coating but worse than the corrosion resistance of the Ti-1Al-1Mn titanium alloy (Fig.3).
Fig.3. Polarization curves of the Ti-1Al-1Mn titanium alloy, an Ni(P) coating and a (Ti,Ni),P + Ti3P + (Ni,Ti,Mn,Al) composite layer formed on the titanium alloy, determined in a 0.5M NaCl aqueous solution.

The surface treatments employed increased significantly the frictional wear resistance of the titanium alloy (Fig.4). The Ti-1Al-1Mn alloy in its starting state was seized as early as after a 10 min test under a unit load of 100MPa, whereas after the same time the Ni(P) layer underwent spalling.

![Graph showing wear resistance comparison](image)

Fig.4. Wear resistance of the (Ti,Ni),P+Ti3P+(Ni,Ti,Mn,Al) composite layer compared to the wear resistance of the Ti-1Al-1Mn alloy.

The (Ti, Ni),P layer has a good biocompatibility with human fibroblasts, expressed as the high fibroblast proliferation (Fig.5) and the lack of dead cells in the population. Statistical analysis showed the statistically significant difference (p<0.05) in proliferation and number of dead cells in fibroblasts culture on Ti-1Al-1Mn vs Ni(P), vs (Ti,Ni),P.

![Graph showing cell proliferation and death](image)

Fig.5. Fibroblast proliferation and the number of dead cells present in the culture on a Ti-1Al-1Mn titanium layer, a (Ti, Ni),P layer and an Ni(P) coating.
In the case of the composite layer, an X-ray microanalysis shows no titanium and nickel ions in the cells and in the incubation fluids extracted from the culture, whereas the cells cultured on the Ti-1Al-1Mn titanium alloy and on the Ni(P) coated samples, as well as the incubation fluids, contained titanium and nickel ions, respectively, as early as after 6 days of the cultivation [9].

4. Conclusions

By combining chemical electroless nickel deposition and a glow discharge enhanced treatment, we can produce composite layers of the (Ti,Ni),P+Ti3P+(Ni,Ti,Mn,Al) type on titanium alloys. The layers have a diffusion character, their surface hardness is about 1200HV0.05 and they show a good resistance to corrosion and frictional wear. Their biocompatibility is better than that of the Ti-1Al-1Mn alloy and they prevent the release of metal ions from the titanium alloy. Therefore we can conclude that they are suitable to be applied as biomaterials.

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References