Abstract: The purpose of present paper is to investigate the corrosion behavior of laser melted surface layers of austenitic stainless steel, immersed into physiological solution. The samples are made of Ch18N10T GOST (AISI 321, EN X6CrNiTi 18-10) steel and their surface is melted by continuous CO2 laser. Then they are polished to different roughness grade and immersed into Ringer’s solution at 37°C temperature for 90 days. The corrosion behavior is investigated by measuring the electrode potential, visual, micro-structural and phase analysis through optical microscopy and XRD-analyzer. The initial mono-phase austenitic microstructure and its morphology change after Laser Surface Melting (LSM). The melted surface layer consists of austenite with dendrite morphology and delta-ferrite in the dendrites core. The delta-ferrite quantity is minimal on the surface and maximal in the melted pool bottom. The nonmetallic inclusions, typical for the initial microstructure, could not be seen in the melted layer. The electrode potential of the initial metal sample and the laser melted layers is about 190-250mV at 37°C temperature. This value doesn’t change during the tested period. Different roughness grades do not considerably influence the electrode potential. The visual and micro-structural analysis shows there are no changes in the microstructure of the subsurface layer. Since the LSM leads to refining of the surface layers and the second phase (delta-ferrite) quantity on the surface is minimal, this type of treatment of the austenitic steel does not bring to considerable changes of its corrosion behavior.

Keywords: LASER MELTING, AUSTENITIC STAINLESS STEEL, CORROSION RESISTANCE, RINGER’S SOLUTION

1. Nomenclature

- $\lambda$ – laser wave length [μm];
- $d$ – laser beam spot diameter [cm];
- $V$ – scanning speed [cm/s];
- $N_s$ – power density [W/cm²];
- $E_v$ - volume energy density [J/cm³];
- $E_{cor}$ – corrosion potential [mV];
- $A$ - austenite;
- $F$ - ferrite;
- $M_Z$ – melted zone;
- $H_AZ$ – heat affected zone;

2. Introduction

Austenitic stainless steel is the first metallic biomaterial which was adapted to be implanted in human body. This group of biomaterials is in common use mainly as short term implants, for example in orthopedic surgery, dental surgery and thoracic surgery [1, 2]. The chemical composition ensures paramagnetic, austenitic structure, determining good corrosion resistance and biocompatibility. In addition to the mono-phase structure, the steel corrosion resistance is determined by the presence of $\delta$-ferrite and elimination of different inclusions, especially MnS, in the surface layer. The research of Sen Yang et al. [7] also shows that laser melted surfaces possesses higher intergranular corrosion resistance owing to the Cr redistribution.

The up to date investigations are mainly done in fluids, used in chemical and mechanical industry, while data for the corrosion resistance of laser treated surfaces of stainless steels in human body fluids are relatively scarce. The purpose of present paper is to investigate the corrosion behavior of laser melted surface layers of austenitic stainless steel, immersed into physiological solution.

3. Experimental Methods

Laser Treatment

Prismatic samples (10mm x 30mm x 100mm), made of steel AISI 321 (EN X6CrNiTi 18-10) with chemical composition shown in Table 1, were used in the experiments. The samples were manufactured by milling, followed by laser surface melting, grinding and polishing to different roughness grade. The surface treatment was realized by continuous wave (CW) CO2 laser (wave length $\lambda=10.6μm$, initial power $N=1.2kW$). Laser treatment was realized with regimes (Table 2), ensuring different melting depth of the surface layer. Single pass was performed in the middle of the sample’s 30mm side. The technological parameters were defined using the formulae:

$$N_s = 4N / \pi d^2.$$  \hspace{1cm} (1)

$$E_v = N_s / V.$$  \hspace{1cm} (2)

Where: $N_s$ – power density [W/cm²]; $d$ – laser spot diameter [cm]; $E_v$ – volume energy density [J/cm³]; $V$ – scanning speed [cm/s].

Corrosion Test

The experiments were carried out by immersing of the samples in Ringer’s solution (9g/l NaCl, 0,42g/l KCl, 0,48g/l CaCl2, 0,2g/l NaHCO3) for 90 days in temperature 37±1°C. The corrosion potential of the laser melted layer and the base metal was measured.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 321</td>
<td>0,075</td>
<td>18,20</td>
<td>10,85</td>
<td>0,98</td>
<td>1,82</td>
<td>0,042</td>
<td>0,012</td>
<td>0,52</td>
</tr>
</tbody>
</table>
three times in every 30 days. Because the surface was partially treated it was impossible to measure corrosion resistance according to the ASTM F 2129 standard, especially designed for implants corrosion testing [8, 9]. Since the width of the laser melted layers was 3-4mm the thin electrode was needed. The measurements were done by device for measuring of the corrosion potential and electromotive voltage of metal objects in the mouth Dentotest-Six. The first electrode was connected with the laser melted layer, while the second one was immersed into the solution on 2-4 mm distance from the sample. The macro- and microstructural analysis was made by optical microscopy.

4. Results and analysis

Results obtained

The initial steel microstructure, before laser treatment, consists of austenite characterized with clearly manifested grain boundaries, typical sliding planes and twinning (Fig.1). Great number of small size non-metallic inclusions exists along the grains boundaries.

![Fig.1 Microstructure of AISI 321 steel.](image)

![Fig.2 Macrostructure of laser melted layer – 1 and base metal - 2 of AISI 321 steel.](image)

Particular large non-metallic inclusions with prolonged shape and transgranular location can be seen.

The chosen regimes of laser treatment result in melting of the surface layer on 0.2-0.4mm depth (Fig.2). Our previous investigations show that the microstructure of the melted layer possesses dendrite morphology, consisting of austenite and δ-ferrite

![Fig.3 Microstructure of base metal and laser melted layers after 3 months test in Ringer’s solution: a) - subsurface of the base metal; b) and c) – subsurface of the melted layers; d) and e) – bottom of the melted layers. (Ev=34x10^3 J/cm³ – b) and d); Ev=28,3x10^3 J/cm³ - c) and e).](image)
The δ-ferrite is situated in the dendrite cores and its quantity is larger in the melted pool bottom comparing to the surface. Non-metallic inclusions could not be seen in the melted zone (Fig.3).

The macro-structural analysis could not reveal visible changes on the surface of the base metal and the laser treated samples as well, after 90 day immersion in Ringer’s solution. In large magnification on the surface of all samples are observed precipitations from the solution, mainly carbonates [8]. The higher roughness of the surface is a precondition for more precipitations (Fig.4).

The corrosion changes in the microstructure of the subsurface and inside the base metal and the laser melted layers were not established by optical metallography (Fig.3).

The average corrosion potential $E_{cor}$ of the base metal lightly changes in one month: from -43mV to +10mV (Fig.5). The corrosion potential of the laser melted layers is higher than this of the base metal. In two month’s tests the average corrosion potential $E_{cor}$ of sample 1 is +173mV, this of sample 2 is +155mV, while of the polished sample 3 it is +141mV. In one more month these values are higher with 20-50mV, but the average corrosion potential of the polished sample remains lowest. As a whole, the corrosion potential values of all samples are in the referenced interval for austenitic steel from -380mV to +300mV [9].

**Discussion**

Stainless steel is mainly attacked by four types of corrosion: galvanic, pitting, crevice and intergranular [3, 4]. This steel is particularly predisposed to pitting corrosion due to inclusions of dissimilar material, trapped in the metal during the manufacturing process. These impurities may initiate pitting corrosion in relation to the grain boundary. Intergranular corrosion is a form of galvanic corrosion due to impurities and inclusions in the alloy. Stainless steels, if improperly heat treated after fabrication, may corrode by this mechanism, owing to a relative depletion of chromium from the regions near the grain boundaries. Crevice corrosion is a form of local corrosion due to differences in concentration of electrolytes or changes in pH in a confined space. The narrower and deeper the crack is, the more likely is crevice corrosion to start.

In our experiments, we obtained higher corrosion potential of laser melted layers, comparing to the base metal, which most probably is a result of the new-formed dual phase structure. Because of the small δ-ferrite quantity, corrosion potential is still in the reference values. Besides the laser surface melting leads to refined microstructure, free of inclusions, thus eliminating main reasons for pitting and intergranular corrosion. Polishing decreases the possibility for keeping the electrolyte on the surface grooves, increasing the resistance to crevice corrosion. As a result, corrosion potential of the polished sample is the lowest during the whole test period. Since the main reasons for more types of corrosion were eliminated, corrosion changes on the samples’ surfaces were not observed.

**Fig. 4** Surface of the base material – a) and laser melted layers – b) and c) after 3 months test in Ringer’s solution (Ev=34x10³ J/cm³ – b) and Ev=28,3x10³ J/cm³ - c).

**Fig. 5** Corrosion potential of AISI 321 steel and laser melted samples after 2 and 3 months test in Ringer’s solution: 1)-Ev=31,7x10³ J/cm³; 2)-Ev=34x10³ J/cm³ and 3)-Ev=28,3x10³ J/cm³.
Conclusions

Investigation of the corrosion behavior of laser melted layers of AISI 321 steel in Ringer’s solution shows that the laser melting of the surface leads to refining, lack of non-metallic inclusions and forming of dual phase structure, consisting of austenite and δ-ferrite. As a result, the average corrosion potential of the melted layers is higher than this of the base metal. It is in the range from +163mV to +223mV, since the polished sample possesses the lowest value. Due to the small δ-ferrite quantity the average corrosion potential is in the reference values. Optical metallography does not reveal corrosion changes in the microstructure of the surface and inside the base metal and the melted layers as well.

Since the laser surface melting leads to eliminating of the main reasons for the more types of corrosion, this type of treatment of the austenitic steel does not bring to considerable changes of its corrosion behavior.

References

8. R.A.Corbett, Laboratory Corrosion Testing of Medical Implants, ASM International, 7p.;