Preliminary Results on the Surface of a New Fe-Based Metallic Material after “In Vivo” Maintaining

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Abstract. A new Fe-based alloy was obtained using UltraCast melting equipment. The alloy, after mechanical processing, was implanted in five rabbit specimens (with respect for the “in-bone” procedure). After 30 days of implantation the samples were recovered and analyzed by weight and surface state meanings. Scanning electron microscopy technique was used to determine the new compounds morphology from the metallic surface and X-ray dispersive energy spectroscopy for chemical analyze results. A bond between the metallic material and biological material of the bone was observed through increasing of sample weight and by SEM images. After the first set of tests, as the samples were extracted and biologically cleaned, the samples were ultrasonically cleaned and re-analyzed in order to establish the stability of the chemical compounds.

1. Introduction
Progress in materials science and engineering, particularly in the areas of processing and thermo-mechanical treatments of metallic materials allow them structural adjustment [1-6]. Increasingly growth in higher expectations of society for a higher level of life rushed forward biomaterials and especially new technologies for producing implants with very good clinical performance. Implants paradigm to be inert and corrosion resistant in these moments is caused by the emergence and development of new classes of materials, that of degradable biomaterials [7-10].

Some special clinical problems (illness / injury) only require temporary support for healing. This support can be provided only temporary degradable materials that allow the implant to degrade gradually when fully function is fulfill. The concept of biodegradable medical applications is known as the "biodegradable sutures". However, degradable implants, especially those made of metallic materials, can be considered a new concept effectively responding paradigm that "metallic biomaterials must be corrosion resistant" [11-14]. The alloys based on Fe or Mg is two classes of metals which have been proposed for applications, such as biodegradable materials. Some of the Mg based alloys have been dealt with Mg-Al, Mg-Ca and M- RE. In the case of alloys based on Fe were considered pure Fe and Fe-Mn. They are mostly proposed for cardiovascular applications [15-18]. The general concept is simple degradable biomaterials as their name, some implants require their presence only temporarily damaged bone to support the healing process of diseased tissue. This temporary...
intervention (implant) is considered in the application only in certain cases such as cardiovascular, orthopedic and pediatric [19-23].

The article presents some experimental results from the analysis of the surface of FeMnSi alloy after a 30 days implantation period in a biological living environment.

2. Experimental

The experimental alloys were obtained using UltraCast furnace (Ar atmosphere) from high purity metals and master alloys.

The in vivo experiments were conducted according to the Faculty of Veterinary Medicine of Iași Ethics Committee guidelines, and ISO 10993-2: 2006 animal welfare requirements, on lots of each five experimental rabbits, males, 12 weeks age and 1000 g average weight, in Agronomic and Veterinary Medicine University (USAMV) Biobase. The experimental rabbits were hosted in individual cages with free water and food access.

Scanning electron microscopy technique was used to determine the new compounds morphology from the metallic surface and EDS technique for chemical analyze results. A SEM VegaTescan LMHII model was used at 30 kV filament power supply. For chemical determinations the preliminary results were obtained using Quantax Bruker EDAX detector and Esprit software. The metallic samples were cleaned in an ultrasound bath with technical alcohol for 60 minutes and re-analyzed by surface point of view. Digital balance was used in order to be weighted the samples and information till milligrams values were modifications appear in 30 days.

3. Results

Two of five FeMnSi implanted samples were analyzed after 30 days of implantation in a rabbit bone with respect to the implantation protocol. The samples were weighed initially before the implantation, after the implantation and after a cleaning session through sonication for 60 minutes in an alcohol bath. Metallic implant information, weight and dimensions, before and after a 30 days implantation period are presented in table 1. By weight point of view, table 1, we observed two situations, first – sample 1 – when the sample is corroded and lose weight before and after sonication and secondly – sample 2 – for similar conditions the sample is corroded but win weight based on the compounds formed on the surface and additional bone tissue from the implantation area.

| Sample 1 before and after implantation (30 days in a rabbit bone) | Length [mm] | Initial width [mm] | Thickness [mm] | Initial weight [g] | After implantation weight [g] | After sonication of the implant [g] |
|---------------------------------------------------------------|-------------|-------------------|-----------------|----------------|-----------------------------|----------------------------------|
|                                                              | 25.3        | 2.45              | 0.45            | 0.2284         | 0.2277                      | 0.2177                           |

| Sample 2 before and after implantation (30 days in a rabbit bone) | Length [mm] | Initial width [mm] | Thickness [mm] | Initial weight [g] | After implantation weight [g] | After sonication of the implant [g] |
|---------------------------------------------------------------|-------------|-------------------|-----------------|----------------|-----------------------------|----------------------------------|
|                                                              | 25.2        | 2.5               | 0.5             | 0.2195         | 0.2305                      | 0.2276                           |

The weight lost by first sample is 0.7 mg and after the sonication process 10 mg of the material is removed from the implant surface as compounds with low stability and almost detached from the surface after the implantation time.

In figure 1 are SEM micrograph of the material surface after implantation period and sonication of the material a) along the implant surface and b) detail of the surface. The images present a corroded surface, at macro and micro scale, with different types of compounds form.

Chemical insights were taken from the implant surface before and after sonication process. Results on distribution of elements Fe, Mn, Si, Ca, P, O and Na are presented in figure 2.
Figure 1. SEM micrograph of the material surface after implantation period and sonication of the material a) along the implant surface and b) detail of the surface.

The elements distributions present the appearance of Ca-P compounds, oxides and before sonication reduced traces of Na, figure 2 a). After sonication a stable oxide layer, figure 2 b), is present on the right side and on the left a metal corroded substrate is observed.

Figure 2. SEM image in centre of the surface after implantation and before sonication stage in a) and after in b) and distributions of elements Fe, Mn, Si, Ca, P, O and Na.

In table 2 chemical compositions from different area are presented. We present the results for chemical composition on a large 4 mm2 area, a reduce 0.25 µm2 area point 1 – from the SEM detail presented in table 2, on another reduced area of 0.25 µm2 area point 2, from the SEM detail presented in table 2, after sonication process on a clean area and on deposited layer, figure 2 b).

All the chemical composition results present corroded areas with formation of new compounds, especially oxides but also compounds with calcium, phosphorus, magnesium and sodium. On macro-scale we observed a high quantity of oxides, C-based and Ca-based compounds (new compounds formed on the metallic surface or biological tissue traces). In point 1 the oxides layer is thinner so a bigger signal for substrate is registered. Manganese element is smaller in all areas and means that Mn compounds from the implanted alloy are prone to corrosion more than Si compounds which keep a higher percentage.
Table 2. EDS results after implantation period before and after sonication process.

| Chemical composition on 4 mm² area | Fe [wt.%] | Mn [wt.%] | Si [wt.%] | O [wt.%] | C [wt.%] | Ca [wt.%] | Na [wt.%] | P [wt.%] | Mg [wt.%] |
|-----------------------------------|-----------|-----------|-----------|---------|---------|-----------|---------|---------|---------|
| After sonication                  | 43.92     | 18.01    | 0.25      | 0.1     | 0.51    | 0.41      | 39.18   | 56.1    | 11.43   |
| Chemical composition on 0.25 µm²  | 75.03     | 46.83    | 0.29      | 0.19    | 0.82    | 1.02      | 19.13   | 41.68   | 2.79    |
| area point 1                       |           |          |           |         |         |           |         |         |         |
| Chemical composition on 0.25 µm²  | 35.6      | 16.7     | -         | -       | -       | -         | 36.71   | 60.09   | 3.3     |
| area point 2                       |           |          |           |         |         |           |         |         |         |
| After sonication                  | 93.03     | 78.16    | 0.33      | 0.28    | 0.8     | 1.34      | 1.88    | 5.51    | 3.64    |
| Chemical composition on the clean | 78.25     | 47.78    | -         | -       | 0.58    | 0.71      | 14.73   | 31.59   | 3.71    |
| area                                |           |          |           |         |         |           |         |         |         |
| Chemical composition on deposited | 38.24     | 15.3     | -         | -       | 0.64    | 0.51      | 48.7    | 68.01   | 6.44    |
| layer                               |           |          |           |         |         |           |         |         |         |
| Error                              | 1.27      | 0.05     | 0.06      | 5.57    | 1.67    | 0.11      | 0.19    | 0.06    | 0.09    |

In point 2 large amounts of oxygen and calcium are observed. After sonication compounds are detached from the surface so we can conclude that in time the degradation of the material continues. After sonication are still stable, in small areas, oxides and small quantities of Ca-P material. After sonication more than 85% of the compounds detach from the surface.

4. Conclusions
Preliminary results after the implantation of a FeMnAl alloy for 30 days in a biological environment are presented using scanning electron microscopy, X-ray energy dispersive analyze and weight measurements. The results present the metallic material surface after implantation period and before and after a cleaning process by sonication. All the surface present corrosion traces and formation of unstable with low adhesion compounds especially oxides and Ca-P compounds. Traces of Na and Mg were also observed on different parts of the surface.

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