Corrosion of Sintered Materials Based on Iron

Petra Slotová
Brno University of Technology
Department of Electrical and Electronic Technology
Brno, Czech Republic
xsloto00@vutbr.cz

Marie Sedlaříková
Brno University of Technology
Department of Electrical and Electronic Technology
Brno, Czech Republic
sedlara@vut.cz

***Abstract*—This paper addresses the topic of biodegradable bone implants. Presently, titanium alloys, known for their ability to reinforce bone structure, are utilized for fracture fixation. Nevertheless, post-healing, their extraction from the body becomes necessary. Biodegradable implants serve the same purpose but undergo gradual degradation upon exposure to bodily fluids. Consequently, the need for additional surgical procedures for their removal is obviated.**

***Index Terms*—biodegradable, corrosion, pH, conductivity, iron, sample**

I. Introduction

This paper deals with Fe-based biodegradable sintered materials and their corrosion. Nowadays, mainly materials based on titanium compounds are used, which have excellent mechanical strength and properties, but after partial healing of the fracture, they must be surgically removed [1].

Biodegradable materials based on inorganic substances, such as iron, magnesium or zinc, could help prevent further surgical intervention in the body. The fracture healing process itself could be much better when using materials that are able to degrade in the body. The bone support will be gradually absorbed by corrosion processes and safely removed from the patient's body. Different compositions of such materials are investigated in different corrosion environments in order to evaluate different properties [2].

Corrosion is a spontaneous, gradual transformation of metals or non-metallic organic and inorganic materials. It arises as a result of a chemical or electrochemical reaction of the basic material with the external environment. It consists of an anodic and a cathodic reaction, which are interconnected and one cannot occur without the other unless an external current is passed through the corroding metal. The anodic reaction represents the oxidation of the metal. The cathodic reaction represents the reduction of oxygen of oxygen dissolved in the electrolyte [3].

II. Preparation of samples

The manufacturing of samples of biodegradable bone implants took place in the following steps. First of all, it was necessary to prepare the material for sintering. The mixture was created by mixing metal powder (Fe) with magnesium (Mg) and with different amounts of polystyrene (PS) for individual samples. The exact composition of the individual samples is written in Table 1. The next step after preparing the correct ratio of the individual samples was the sintering of the material. By sintering, a solid material was created, prepared for insertion into a corrosive environment. Due to the different weight of the individual samples, their dimensions and also the surface area are different. These are irregular blocks that have a width of 1 cm, a height of 0.5 cm and a length of 5 - 6 cm, depending on their weight. Subsequently, a saline solution (0.9% sodium chloride solution, NaCl) was mixed into which the individual samples were inserted. Each sample was immersed in 30 milliliters of solution and it was a static bath. The samples soaked in the solutions were then placed in an environment with a temperature of 37 °C, which had the task of simulating the temperature of the human body [4].

TABLE I
Composition of 4 different samples

Sample composition	
Sample 1	9 g Fe, 1 g Mg, 1.5 g PS
Sample 2	9 g Fe, 1 g Mg, 1 g PS
Sample 3	9 g Fe, 1 g Mg, 0.5 g PS
Sample 4	9 g Fe, 1 g Mg, 2 g PS

III. Measurements

The aim of the measurements was to monitor the development of changes in pH and conductivity of individual solutions caused by the corrosion processes of the samples. Thanks to the monitoring of these changes, it is then possible to determine the speed of individual corrosion processes, or to determine the amount of metal released into the body. It is also subsequently possible to estimate whether the amount of metal released is in line with expectations or could have some adverse effect on the human body.

Before the very beginning of the measurements of individual samples, the pH and conductivity values of the saline solution were measured. A pure NaCl solution should have a pH value of around 7. The measurement found a value of around 7.5. As for the conductivity, around 51 mS/cm was measured.

The measurement of individual samples started 10 days after they were placed in the solutions. In the next subsections, the individual measurements are shown in more detail, and it can be seen that the pH and conductivity values of the solution changed very quickly after insertion.

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A. pH measurement

One of the measurements was the measurement of the pH of the solutions. Based on it, it is possible to find out how quickly the corrosion processes take place in individual samples and how the corrosion speed changes itself. From the measurements, it is possible to find out how much metal is gradually degraded and how much remains in the body. Subsequently, it is possible to roughly estimate whether the values are acceptable for the human body or could already be dangerous.

All four samples were placed in a saline solution, which had the task of simulating the environment of the human body and was kept at a temperature of 37 degrees Celsius for the entire time. The first measurement took place after 10 days of being placed in the solution and was subsequently repeated approximately every week for 3 months.

Changes in pH values are illustrated in Figure 1. It can be observed that at the beginning, when the surface of the material is clean, faster oxidation occurs. As a result, water begins to be reduced and hydrogen and OH- are formed, resulting in alkalization. However, the released OH- will begin to gradually bind to iron, which will cause the pH values to decrease again. For a closer overview, Table 2 also summarizes the actual numerical values from measurements at certain time intervals.

TABLE II
MEASUREMENT OF PH SOLUTIONS

pH of solutions						
Number of days	***10***	***19***	***33***	***54***	***68***	***91***
Sample 1	11.34	11.18	10.71	10.77	10.67	10.35
Sample 2	10.76	10.66	10.54	10.44	10.42	10.02
Sample 3	10.74	10.71	10.47	10.38	10.42	9.97
Sample 4	11.30	11.28	1071	10.75	10.71	10.26

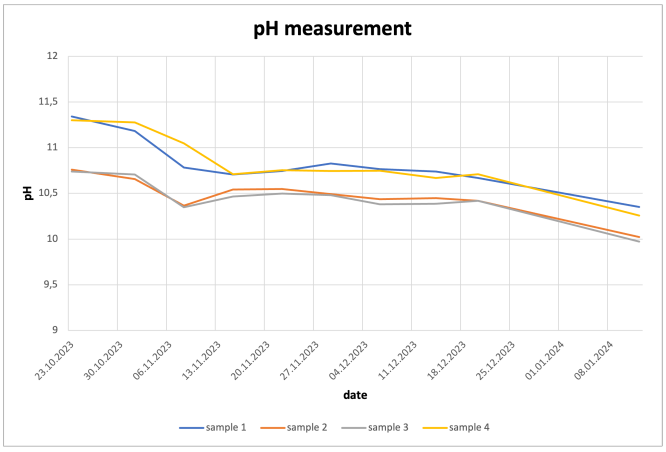

Fig. 1. Difference in corrosion solution pH depending on time.

B. Conductivity measurement

The second of the measurements was the measurement of the conductivity of the solutions. The measurement was similar to that of pH. The first measurement also took place after 10 days from being placed in the solution and then repeated approximately every week for 3 months.

Changes in conductivity values are shown in Figure 2. The curves have a decreasing character of conductivity, which is caused by the process of precipitation of ions in the solution. It can be seen that while in sample 4 there was a rather sharp decrease in sample 2, the decrease in wonder was significantly slower. Table 3 is prepared for a closer overview of the values.

TABLE III
MEASUREMENT OF CONDUCTIVITY SOLUTIONS

Conductivity of solutions [mS/cm]						
Number of days	***10***	***19***	***33***	***54***	***68***	***91***
Sample 1	11.56	11.79	11.56	11.24	11.05	10.93
Sample 2	11.37	11.35	11.17	10.80	10.61	10.53
Sample 3	12.06	12.02	11.75	11.46	11.11	10.97
Sample 4	11.13	11.30	10.96	10.58	10.05	10.03

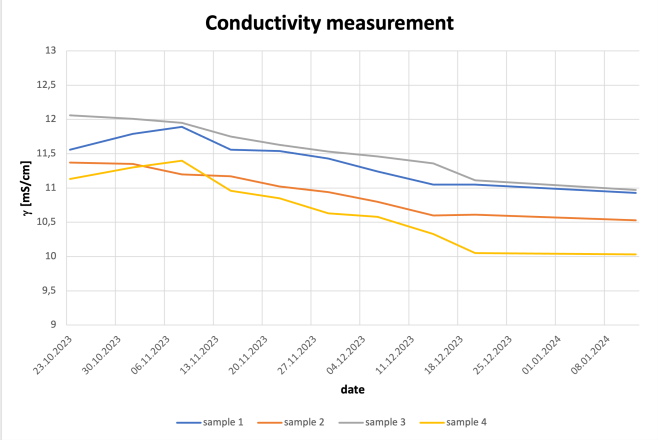

Fig. 2. Difference in corrosion solution conductivity depending on time.

IV. ENERGY DISPERSIVE X-RAY ANALYSIS

Energy dispersive X-ray analysis, shortly EDAX, is an analysis that is used to determine the occurrence of elements in a sample and their percentage representation. The principle of this method is based on the generation of X-ray radiation, which is created by the impact of the primary beam of electrons on the examined sample. When an electron beam hits the sample, elastic scattering can occur, in which the beam of primary electrons is deflected by the force of the nucleus, its energy is reduced and the energy difference is emitted in the form of continuous radiation. In an inelastic collision, the electron is excited to a higher level and the atom goes into an unstable state. To ensure stability, the transition of an electron from a higher level to the place of a freed electron occurs, and the energy difference of these levels is emitted in the form of characteristic X-ray radiation. In energy dispersive X-ray analysis, there is an effort to detect characteristic radiation, because this radiation contains a narrow spectrum of energies and an element can be determined based on them [5].

EDAX analysis was performed before placing the samples in the solution (before corrosion) and 96 days after placing the samples in the saline solution (after corrosion). The tables below compare the values obtained from the analyzes for individual samples. An important role in determining the elemental composition could be played by the area from which the elemental analysis was made.

A. EDAX analyses of Sample 1

The analysis of Sample 1 before soaking in NaCl showed that the most abundant element in the sample was iron. The next element that was found was carbon. It probably stayed there as the rest of the foam, which was made of polyurethane material. The amount of carbon was almost the same as the amount of magnesium. After wetting, the elemental composition changed. The amount of iron has decreased, which means that iron leaks out of the sample during corrosion. The amount of oxygen increases after wetting, which could be expected. Chlorine is also present in the sample, which is caused by the NaCl solution. The exact quantities are given in Table 4 and the composition of the sample elements is shown in Fig. 3.

TABLE IV
PERCENTAL AMOUNTS OF ELEMENTS PRESENT IN SAMPLE 1

Sample 1		
Elements	**Sample 1 [%]**	**Sample 1 NaCl [%]**
Iron	64.73	55.00
Carbon	14.75	7.00
Magnesium	14.71	15.63
Oxygen	5.81	21.81
Chlorine	-	0.57

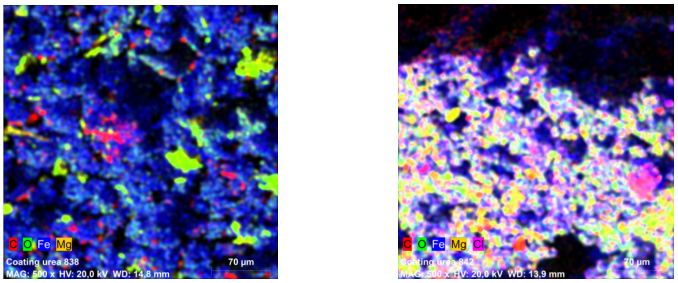

Fig. 3. Distribution of elements in Sample 1 before and after wetting in NaCl

B. EDAX analyses of Sample 2

For Sample 2, the analysis before wetting showed similar results as for Sample 1. The most represented element is iron, followed by carbon. After soaking in the solution, the amount of iron and carbon decreases again. The amount of magnesium and oxygen increases, and a trace amount of chlorine also appears. The exact amount of individual elements is again shown in Table 5, and the composition of the elements of the sample before soaking in the solution and after soaking is shown in Figure 4. In the individual sample images it can be seen that the individual elements are evenly distributed in each pattern.

TABLE V
PERCENTAL AMOUNTS OF ELEMENTS PRESENT IN SAMPLE 2

Sample 2		
Elements	**Sample 2 [%]**	**Sample 2 NaCl [%]**
Iron	70.48	48.35
Carbon	13.67	6.54
Magnesium	10.86	19.18
Oxygen	4.98	24.97
Chlorine	-	0.96

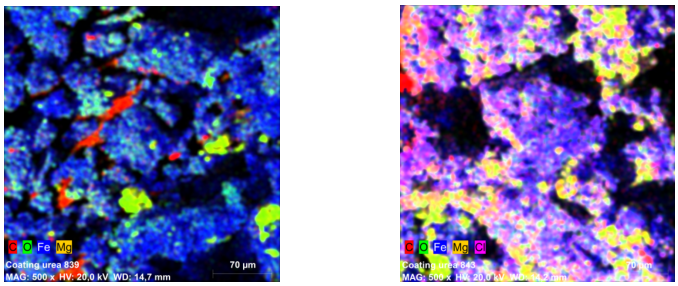

Fig. 4. Distribution of elements in Sample 2 before and after wetting in NaCl

C. EDAX analyses of Sample 3 and Sample 4

EDAX analysis of Samples 3 and 4 turned out very similar to the previous two. In any case, iron had the largest presence, the amount of which decreased after soaking. The only difference is that in Sample 3, chlorine elements were not found after soaking as in the previous two. On the other hand in Sample 4, after soaking, not only chlorine, but also sodium was recorded, both appeared there due to NaCl solution. The exact amounts of individual elements are again clearly shown in Tables 6 and 7.

TABLE VI
PERCENTAL AMOUNTS OF ELEMENTS PRESENT IN SAMPLE 3

Sample 3		
Elements	**Sample 3 [%]**	**Sample 3 NaCl [%]**
Iron	60.27	56.92
Carbon	4.98	6.43
Magnesium	25.33	19.61
Oxygen	9.42	17.04

TABLE VII
PERCENTAL AMOUNTS OF ELEMENTS PRESENT IN SAMPLE 4

Sample 4		
Elements	**Sample 4 [%]**	**Sample 4 NaCl [%]**
Iron	78.69	55.43
Carbon	13.97	719
Magnesium	5.25	16.14
Oxygen	2.08	19.45
Chlorine	-	0.69
Sodium	-	1.1

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CONCLUSION

This work is primarily focused on the long-term monitoring of the degradation of samples in physiological solutions. Conductivity measurement, pH measurement and EDAX analysis were used for qualitative and quantitative assessment of degradation. Four different samples that differed in the amount of polystyrene were examined and compared. It can be clearly seen from the measured curves that both pH and conductivities have a decreasing character. From the EDAX analysis, it is possible to say that the iron really dissolves and decreases with time. In the individual images of the samples, it can be seen that the individual elements are evenly distributed in each pattern. In conclusion of this work, it can be said that iron-based materials containing magnesium and polystyrene really show a relatively satisfactory rate of degradation. However, it is necessary to observe these measurements over a longer time horizon and find out how they will behave after a longer period than three months.

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