Electrochemical behaviour of biomedical magnisium in sbf

Magnesium is a biogene element which is present in the tissues of all organisms. It is a part of a molecule of a green pigment of plants – Chlorophyll, which participates in a mineral exchange, activates fermental processes in an organism, increases drought resistance of plants. Bioluminescence and some other biological processes occur with the participation of Mg+ ions.

Magnesium arrives to an organism of animals and human beings with food. Daily need of magnesium for a person is 0. 3-0. 5 g. The organism of the average person (with body mass of 70 kg) has about 19 g of magnesium.

Magnesium and magnesian alloys possess rather low corrosion stability because of high electronegative potential and insufficient protective qualities of a natural oxide film. The processes with the prevalence of oxygen depolarization proceed under a thin film of moisture and in atmospheric conditions. In the distilled water oxygen and hydrogen depolarization has a commensurable value. The process goes with purely hydrogen depolarization in the salty solutions. Magnesium and its alloys do not possess sufficient stability in the majority of inorganic environments.

They are steady in the solutions of chromic acid and its salts, in the solutions of hydrofluoric acid, its salts, and alkaline solutions. A low electrode potential and instability of a protective oxide film in neutral and acid solutions cause very big speeds of magnesium corrosion and its alloys in these environments. The speed of corrosion sharply falls in alkaline solutions owing to the increase of stability of a protective film and a simultaneous reduction of hydrogen ions concentration. The speed of corrosion increases with the

temperature raise and depends on the alloy structure. 1) Open circuit potential evaluation The corrosion of magnesian alloys in atmospheric conditions depends on the atmosphere of gases and salts, on the duration of a stay of moisture's film on the surface and speed of its evaporation. The greatest speed of corrosion is observed in the industrial areas, the smallest – in rural areas.

The products of magnesium corrosion have approximately the following structure: 61. 5 % of MgC03-3H20; 26. 7 % of MgS04. 7H20; 6. 4 % of Mg (OH) 2; carbonaceous substances ~2. 5 %.

" When the magnesium alloy is exposed to the corrosion medium, chemical dissolution together with electrolyte penetration results in spontaneous corrosion on the entire surface, resulting in the formation of corrosion products, including magnesium hydroxide and magnesium phosphate" (Y. Xin et al.: 2007). The corrosion stability of magnesium of a high purity is reduced by the vast majority of metal impurities and alloying additions being cathodes in relation to magnesium. In the environments, in which the process of corrosion proceeds with mainly hydrogen depolarization, a strong decrease of corrosion stability is observed under the influence of impurity with a low overstrain of hydrogen: Fe, Ni, Co. The metals with a high overstrain of hydrogen, e.

g. Zn, Cd, Al are less dangerous. Each impurity has the limit of its contents; the corrosion stability of magnesium sharply falls. All metals reduce the corrosion stability of magnesium in environments in much smaller degree, the process proceeds with the prevalence of oxygen depolarization in

atmospheric conditions. Some increase of the corrosion stability of magnesium (? = 60 against ? = 45) at the preservation of a rather high superficial density was observed in magnesium solution in the presence of a salty fluoride additive.

Thus, the features of electrochemical behavior of magnesium and its alloys in the solutions of moderately acid phosphates are caused by the change of a surface condition of the studied objects which are the result of a difficult adsorbtion-chemical interaction with the components of solution. " The hydrogen evolution rates and corresponding degradation rates were monitored as a funcion of immersion time. The average degradation rates after immersion in SBF at about 37 °C for 7 days were calculated by means of weight loss and hydrogen evolution. In the hydrogen evolution method depicted in Fig. 1, the hydrogen evolution volume was measured, and the degradation rate was deduced from the reaction below: $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$ " (Y. Xin et al.

: 2007). where ? E is tension (potential difference) attached to an electrochemical cell, ? I – a current proceeding through a cell. Generally enclosed tension of E and current of I have a vector nature. For the communication description between E and I with a view of convenience instead of the system of the linear integro-differential equations harmonious functions are replaced them with fazor ones which allow defining the amplitudes of rotating vectors of tension and a current, located in the complex planes. where ? E is an amplitude maximum.

Fazor represents a rotating vector of E. The sinusoidal tension can be expressed as E = ? E * sin ? t, where ? = 2? f , E is a current (instant) value of the size of tension, and ? E – its maximum amplitude. This size can be defined as a projection to a zero axis of a polar chart, where E fazor is a rotating vector describing sinusoidal fluctuations of tension. It is usually desirable to establish the interrelation between tension and a current in a chain. In the most cases, the current is also described by sinusoidal function and has the same ? frequency, but differs from tension by an amplitude and a phase (being late or advancing on a phase). Expression for a current can be written down as follows: I= ? I • sin (? t + ?).

2) Electrochemical impedance spectroscopy The properties of various physical, chemical, electrochemical and many other systems are convenient for studying using observation over their response to a weak external influence. The impedance method allows making it with a high efficiency. It was used as one of the main methods of research of electrochemical objects for the last decades. In comparison with the other electrochemical methods, this method provides the highest accuracy for exclusively wide range of frequencies of an influencing signal and gives extensive information, both about the kinetics of electrochemical processes and about the properties of a surface and the volume of a studied object. The method at which the impedance of an electrochemical cell or an electrode is measured as function from frequency is called electrochemical impedance spectroscopy (EIS). The electrochemical circuit can be described by two ways: on the basis of theoretical consideration of the processes and creation of a physical model, and by designing of the electric equivalent circuit from the elementary

elements, first of all, resistance (resistors) and capacities (condensers) which behave like cells.

The impedance spectroscopy plays an enormous role in electrochemical and material researches of magnesium. It is more exact in all researches where the phenomena of a charge transfer, the phenomena on the interphase borders, specific adsorption, processes of oxidation restoration and many other things take place. Undoubtedly, with the advent of modern measuring systems combined with personal computers and an automation equipment of experiment, the possibility of impedance spectroscopy increases repeatedly. However, it is always necessary to take into consideration exclusive complexity of the the studied systems, capable of finding the most various responses depending on the nature of a sample and a set of experimental parameters. Though measuring devices were not perfect, the crucial role belongs to an experimenter. He guarantees an adequacy of interpreetations and is responsible for it.

3) Polarization Polarizing ability of Mg2 + ion is low, and magnesium concedes to the majority of metals according to the size factor of polarization which quantitatively characterizes ion deformability. Therefore, the complex compounds of magnesium are unstable and formed usually only in the alkaline environment. The warmth of formation of some compounds of magnesium is presented below: Table 1. The warmth of formations of some compounds of magnesium. From the provided data it can be said that the warmth of formation of similar derivative of beryllium and magnesium are

close at rather small volumes of metalloid atoms (F, O, N) and are strongly different at big (Cl, Br, I, S).

This correlation shows the low polarization ability of magnesium. Conclusion According to the researches described in two articles called " Corrosion behavior of biomedical AZ91 magnesium alloy in simulated body fluids" and " Degradation behaviour of pure magnesium in simulated body fluids with different concentrations of HCO", it is possible to conclude that the corrosion behaviour of magnesium soaked in SBF showed that their rates are very high during the exposure to the solution, later they decrease and at last stabilize during the following two days. In atmospheric conditions, especially in the presence of moisture, magnesium quickly enough corrodes. The impurities of iron, nickel, cobalt and copper sharply reduce corrosion stability of magnesium and its alloys. Magnesium considerably corrodes in simulated body fluids and in 3 % solution of chloride natron and its corrosion speed strongly increases with the temperature increase and concentration.

The diluted mineral acids strongly affect magnesium. Magnesium and its alloys considerably corrode in the majority of organic acids. " Pure magnesium is not sensitive to pitting corrosion in all the three SBFs. Higher concentration of HCO_3^- can effective slow down corrosion rate due to promoting precipitation of protective carbonates. HCO_3^- upto 27 m mol/L can dramatically enhance corrosion potential and induce rapid surface passivation behavior. Therefore, in order to acquire more accurate corrosion performance of Mg-based implants, it is suggested to use SBF with HCO_3^- concentration of 27 m mol/L" (Y.

Xin et al.: 2011).