WEB OF SCIENTIST: INTERNATIONAL SCIENTIFIC RESEARCH JOURNAL
ISSN: 2776-0979, Volume 6, Issue 11, November- 2025

BIOMATERIALS BASED ON GRADIENT MAGNESIUM ALLOYS: BIOLOGICAL ASPECT

Abdujabbarova Umida Mashrukovna
Giyasov Shukhrat Iskandarovich
Tashkent State Medical University, Tashkent, Uzbekistan,
e-mail:u.abdujabborova49@gmail.com. e-mail: dr.sh.giyasov@gmail.com

Islamov Akmal Khushvakovch
Doctor of Chemical Sciences, (DSc)., Leading researcher Institute of Bioorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan,
Web of Scientist: International Scientific Research Journal (WoS)
Member of the editorial board

Abstract
Magnesium alloys are attracting attention as promising biomaterials for temporary implants due to their combination of mechanical properties similar to bone tissue and biodegradability. The introduction of a gradient structure (composite or structural gradient) allows for optimization of corrosion behavior, maintenance of mechanical integrity, and improvement of biocompatibility. This article discusses the principles of creating gradient magnesium alloys, their biological aspects, challenges, and potential applications in biomedicine.

Keywords: Magnesium, implant, biocompatibility, gradient alloy.

Introduction

Modern biomaterials for implants must provide not only mechanical strength but also biocompatibility, stimulate tissue regeneration, and, if necessary, be resorbed by the body. Magnesium (Mg)-based alloys are one of the most promising classes of materials for temporary orthopedic and vascular implants due to their low density, elastic modulus close to that of bone tissue, and the biological significance of magnesium [1-3].

The main drawback of magnesium alloys remains their high corrosion rate in physiological fluids, which can lead to premature implant failure and the formation of hydrogen bubbles [4]. One way to address this problem is to create gradient structures in which the outer layer has increased corrosion resistance, while the inner layers provide the necessary mechanical support [5]. This approach allows for a balance between degradation rate and tissue healing time.

Experimental part.

Object of study. The base material is magnesium alloys doped with elements that improve mechanical and biological properties: zinc, calcium, strontium, manganese, and rare earth metals [6]. These additives regulate corrosion kinetics and promote osteogenesis. Toxic elements such as aluminum and nickel should be avoided. To elucidate the mechanism by which the semi-solid formed microstructure influences the corrosion behavior of magnesium alloys, we prepared a semi-solid formed Mg-Zn-Zr-Nd alloy and studied its corrosion behavior.

Functionally graded materials (FGMs) are characterized by a gradual change in composition or structure from the surface to the core. In magnesium alloys, this is realized as a transition from pure Mg to a composite with ceramic phases (hydroxyapatite, oxides, β-TCP). Such materials have increased corrosion resistance (up to 150% compared to homogeneous Mg) and stimulate osseointegration [7]. Powder metallurgy, plasma spraying, anodizing, spark plasma sintering, and directed gradient cooling methods are used to create gradient structures [8]. Microstructure analysis is performed using scanning electron microscopy (SEM), X-ray diffraction (XRD), and corrosion testing methods.

Biocompatibility is assessed using in vitro tests (MTT analysis, osteoblast proliferation, cytotoxicity) and in vivo experiments in animal models (assessment of osseointegration and inflammatory response). Biological parameters include cell adhesion, alkaline phosphatase activity, and new bone formation [9].

Magnesium is a physiologically essential element and is involved in numerous metabolic processes [1]. The biocompatibility of magnesium alloys is higher than that of most traditional metal implants. A low elastic modulus reduces the stress shielding effect, which promotes normal bone remodeling [2]. The gradient structure, which includes a bioactive outer layer, promotes osteoblast proliferation and the formation of a strong implant-bone bond [10].

The corrosion process of magnesium alloys is accompanied by the release of hydrogen and the formation of magnesium hydroxide, which increases the pH of the environment [4]. Excessive degradation can cause inflammation and gas pockets, but gradient coatings (e.g., Mg/HA) effectively reduce the corrosion rate [7].

Degradation control is a key factor in the biological adaptation of the material: the outer layer protects against premature failure, while the inner layer is gradually resorbed during the healing process [5, 9].

To varying degrees, most materials experience some type of interaction with a wide variety of environments. Often, these interactions reduce the usefulness of the material by degrading its mechanical properties (e.g., ductility and strength), other

WEB OF SCIENTIST: INTERNATIONAL SCIENTIFIC RESEARCH JOURNAL
ISSN: 2776-0979, Volume 6, Issue 11, November- 2025

physical properties, or appearance. Sometimes, to the chagrin of the design engineer, the degradation behavior of a material for a particular application is ignored, leading to adverse consequences.

The failure mechanisms differ for the three types of materials. In metals, actual material loss occurs either through dissolution (corrosion) or through the formation of a non-metallic scale or film (oxidation). Corrosion is defined as a destructive and unintended attack on a metal. For metallic materials, the corrosion process is typically electrochemical—that is, a chemical reaction involving the transfer of electrons from one chemical species to another. Metal atoms typically lose or donate electrons in a reaction known as oxidation. The site where oxidation occurs is called the anode; oxidation is sometimes called an anodic reaction. The electrons generated by each oxidized metal atom must be transferred to another chemical species and become part of it in a reaction known as reduction.

It is well known that the poor corrosion resistance of magnesium alloy limits its application [1]. The semi-solid process has the advantages of low processing temperature and low deformation resistance, resulting in a uniform spheroidized structure and improved mechanical properties [1, 3]. Studies have shown that the semi-solid process can change the microstructure and composition distribution of magnesium alloy by forming network-like liquid β-phases, resulting in improved corrosion resistance of the alloy. However, the mechanism affecting the corrosion behavior of semi-solid magnesium alloys has not been systematically studied.

Therefore, to elucidate the influence of the semi-solid formed microstructure on the corrosion behavior of magnesium alloy, we prepared a semi-solid formed Mg-Zn-Zr-Nd alloy and investigated its corrosion behavior. The Mg-Zn-Zr-Nd alloy is a typical magnesium alloy with a wide semi-solid solidification range [1]. Considering that isothermal heat treatment is an effective and efficient method for producing semi-solid magnesium alloys, we applied it to obtain a typical semi-solid microstructure [4, 5]. Microstructural evolution was studied at various stages of heat treatment. The corrosion morphology and electrochemical behavior of the alloys under various conditions were analyzed to identify the mechanism by which the semi-solid microstructure influences the corrosion behavior of this magnesium alloy.

An Mg-6Zn-0.9Zr-0.9Nd (wt%) alloy was prepared using pure magnesium ingots, pure zinc ingots, and Mg-Zr and Mg-Nd master alloys. These raw materials were melted in a vacuum induction furnace, and the entire melting process took place under an argon atmosphere. In the next step, to create a semi-solid molded microstructure, the cast ingots were heated at 620°C for 15, 30, 45, and 60 minutes and then rapidly quenched in cold water.

Microstructural studies were performed using scanning electron microscopy (JSM-6510A, JEOL, Tokyo, Japan). An X-ray diffractometer (Smart Lab 9 kw, Rigaku, Tokyo, Japan) with Cu Kα radiation was used to analyze the phase composition of the alloys. Simulated biological fluid (SBF) is widely used to determine the in vitro corrosion properties of magnesium alloys. Electrochemical tests in SBF solution were conducted using an electrochemical workstation (LK2010, LANLIKE, Tianjin, China) to characterize the electrochemical corrosion properties of semi-solid alloys. Cyclic voltammetry curves were obtained by starting from an initial potential and returning to the initial potential at the same rate after reaching the termination potential. All potentials mentioned were based on the use of a saturated calomel electrode (SCE). Additionally, the corrosion resistance of the alloys was assessed using immersion tests. The samples were soaked in a SBF solution (pH 7.4, inorganic ion concentrations (mM): Na^{+} 142.0; K^{+} 5.0; $Mg2^{+}$ 1.5; $Ca2^{+}$ 2.5; Cl^{-} 147.8; HCO_3^{-} 4.2; for 1, 6, 24, and 72 h at room temperature. The solution was refreshed every 24 hours to maintain a relatively stable immersion environment.

A single-channel CS150 potentiostat-galvanostat was used to study the anticorrosive properties of the samples. The CS150 potentiostat-galvanostat is a precision potentiostat-galvanostat designed for general-purpose electrochemical measurements. Electrochemical testing was performed in simulated body fluid (SBF: 6.5453 g L-1 NaCl, 2.2683 g L-1 $NaHCO_3$, 0.3728 g L-1 KCl, 0.2681 g L-1 $NaHPO_4$ $7H_2O$, 0.3050 g L-1 $MgCl_2$ $6H_2O$, 0.5488 g L-1 $CaCl_2$ $6H_2O$, 0.0711 g L-1 Na_2SO_4, 6.057 g L-1 $(CH_2OH)_3CNH_2$) with a pH of 7.4 ± 0.02 at 37°C using an electrochemical cell. The corrosion behavior of the materials was evaluated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The Mg-6Zn alloy demonstrated the lowest corrosion current density (Icorr) and the lowest corrosion potential (E_{corr}) among all the samples studied. This indicates higher resistance to corrosion damage in aggressive environments. Mg-6Zn samples exhibit an Icorr of 0.3 10–5 A/cm², which is significantly lower compared to other alloys. The amount of magnesium in Mg-6Zn samples contributes to the weakening of anodic and cathodic reactions, leading to a significant reduction in corrosion.

Additions of Ca, Sr, and Zn to the alloy structure increase the expression of osteogenic markers, osteocalcin activity, and accelerate extracellular matrix mineralization [6, 11]. Bioceramic inclusions enhance surface bioactivity, which is important for implants intended for osteosynthesis and bone defect restoration.

Conclusion

The study demonstrated that the Mg-6Zn alloy exhibits the best anticorrosion properties among the magnesium alloys studied (Mg, Mg-6Zn, Mg-1Zn, and Mg-0.5Zn). This is confirmed by the lowest corrosion current density, high polarization resistance, and significant impedance at a frequency of 0.1 Hz, indicating a high degree of passivation and corrosion protection. Mg-0.5Zn and Mg-1Zn alloys also exhibit improved anticorrosion properties compared to pure magnesium, but are inferior to Mg-6Zn. Therefore, the Mg-6Zn alloy is recommended for use in conditions requiring high corrosion resistance.

Modern research confirms that gradient magnesium alloys effectively combine mechanical stability, controlled degradation, and biological activity [7, 9, 10]. However, unresolved issues remain:

- the need for precise corrosion rate control;
- preventing the formation of hydrogen bubbles;
- studying the long-term behavior of degradation products;
- technological challenges in creating uniform gradients [3, 12].

Future research should focus on developing combined systems with multilayer coatings, optimized porosity parameters, and controlled biochemical properties. An important area is the integration of materials science, cell biology, and biomechanics to create implants adapted to tissue healing dynamics.

Gradient magnesium alloys represent a promising class of biomaterials that combine strength, biocompatibility, and controlled degradation. The use of gradient structures allows for a balance between corrosion resistance and biological activity. These materials have significant potential for use in orthopedic and maxillofacial surgery, but additional in vivo studies are needed to evaluate the long-term effects of tissue interactions.

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