

Zinc-based Degradable Biomaterials – Limitations and Enhancements

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Nowadays there is a high trend and effort to find a suitable biodegradable metal, whose mechanical properties would be the same or higher to those of currently used biomaterials. Current biomaterials, such as stainless steels, cobalt-chromium alloys, and titanium alloys have superior mechanical properties, machinability, and durability, but are considered nondegradable, and long-term clinical complications may occur. Their biggest disadvantage is that the patient must have undergone a second removal surgery. Therefore, new biodegradable materials have been developed to eliminate the shortcomings of current biomaterials. Magnesium (Mg), iron (Fe) and zinc (Zn) based alloys have been proposed as biodegradable metals for medical application. Iron-based alloys show good mechanical properties compared to magnesium-based alloys. However, both of them exhibit bad corrosion properties, because the degradation rate of magnesium has proven to be high. On the other hand, the degradation of iron-based alloys is too slow in a physiological environment. The corrosion attack of both materials is not typically uniform. Therefore, zinc is proven to be a promising material for this application.

Keywords: Mechanical properties, corrosion properties, biomaterials, biodegradable metals

1 Introduction

Nowadays, there are large range of biomaterials, which are most often used for hard tissue reconstruction and replacement. The most commonly used are titanium and its alloys, stainless steels as well as cobalt-chromium alloys [1]. All these materials are characterized by excellent properties, which include mainly mechanical properties, machinability, and formability, but also economically, their affordability [2]. The usability of those materials is optimal in the cases, where the organism is not possible to regenerate destroyed tissue (age, illness) alone. On the contrary, those materials are not suitable for using them for the children and must be often re-operated in order to prevent the destruction of growing bone. To eliminate such problems, new materials called biodegradable biomaterials have been developed (we can also meet the synonymic concept bioabsorbable metals) [3]. It is a revolutionary biomaterial that is gradually degrading, while still providing the necessary support for complete healing. Thus, in such a case, the patient avoids the sur-

gery that would be necessary for a conventional biomaterial [3, 4]. Graphical processing of the theoretical functionality of biodegradable material is shown in **Fig 1**. The concept of biodegradable materials is simple. The implanted material should provide support until the tissue gradually regenerates [5]. Another very important condition for the biodegradable material is its corrosion resistance. As can be seen in **Fig. 1**, the degradation of the biodegradable implant should be as fast that the mechanical properties do not reach a value of whole system failure [5]. More precisely, the corrosion rate should be as fast as new bone growth. Corrosion resistance is also associated with the fact that not only the material but also its corrosion products should be non-toxic and biocompatible [6]. Until this moment, only the conditions connected with the corrosion process were mentioned. It is obvious that the corrosion process is in the case of biodegradable metals crucial and affects mechanical properties as well as the behavior in the organism. Magnesium, iron, and zinc belong to biodegradable metals group due to fulfilling the basic requirements mentioned above [7].

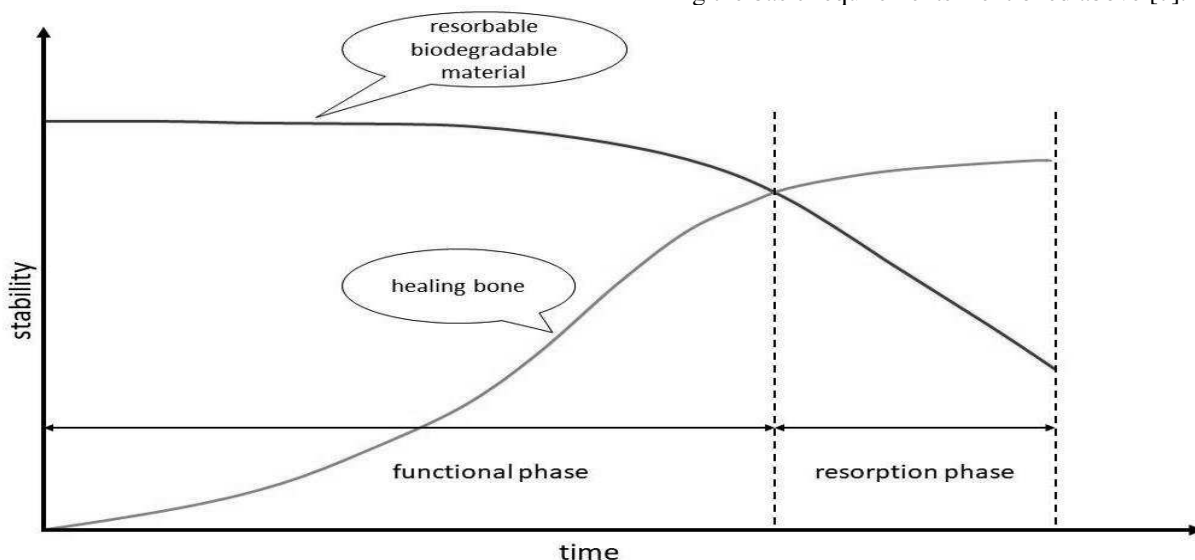
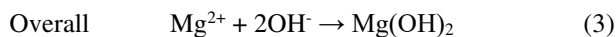
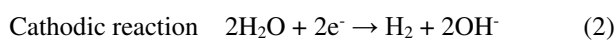


Fig. 1 The theoretical principle of biodegradable material

2 Magnesium

Magnesium has been studied for decades as a biodegradable material [8-12]. One of the first clinical applications of pure magnesium implant was done by Lambotte in 1906 [11]. The results of magnesium research were at this early stage unsatisfactory and pure magnesium platelets were removed due to extensive gas cavities, local swelling and severe pain [12]. According to those observations was found that the corrosion process of magnesium and its alloys is accompanied by the evolution of hydrogen gas and the amount depends on the corrosion rate [10]. The production of high amounts of gas in a short period of time is not desirable for clinical application and may cause significant problems accompanied by the heart or brain damage. The knowledge of the corrosion process is quite important, and it is described by Eq. (1-3).

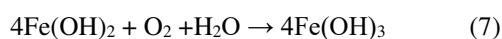
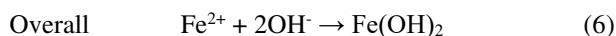
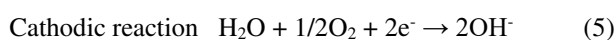
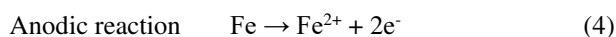


During the corrosion processes, hydrogen gas and also Mg^{2+} are released. Magnesium is commonly contained in the human body and therefore the release of Mg^{2+} is not harmful. The recommended dietary allowances of magnesium is for male in the range 240-420* mg/day and for female in the range 240-320* mg/day (*dependent of age) [3, 13]. If this concentration is exceeded, health complications may occur (for example hypermagnesemia) [14].

3 Iron

Another candidate for a biodegradable biomaterial is iron and its alloys [15]. Iron has better mechanical properties and a slower rate of degradation (in cardiovascular applications).

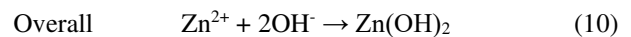
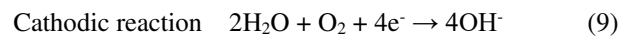
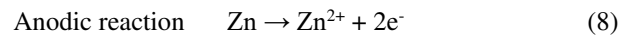
Although iron is contained in the human body to the greatest extent, an overdose of iron may not always be favorable. Iron degrades according to the following Eq. (4-7):



The resulting Fe^{2+} ions may not form the Fe(OH)_x ($X=2$ or 3) and they may accumulate in the cells resulting in toxicity [16]. The literature indicates that the safe concentration of iron, i.e. the recommended dietary allowances, should be approximately 10 mg/day [3, 17]. Therefore, it is necessary for this material to achieve a slower release of Fe^{2+} , resulting in reduction of its concentration and therefore is no longer harmful to the human body. As a consequence, it is impossible to reach the optimal ratio between the corrosion rate and the number of released ions. Another disadvantage, when used in the human body, is that the corrosion products are retained in the tissues for a long time.

4 Zinc

Last but not least, the zinc is also considered as a biodegradable metal [18]. The main advantage is almost ideal corrosion behavior of zinc under the physiological conditions compared to those of pure magnesium and iron. The corrosion rate lies between mentioned metals and the corrosion process is not connected with direct hydrogen evolution [6], as shown in the equation 9.



In addition, the corrosion products are completely bioreabsorbable, which is a crucial parameter for such materials [6]. For these reasons, the following text will refer exclusively to zinc. The zinc is an essential element participating in various biological functions as brain activity or mineralization of bones and is localized especially in the bones and muscles [19, 20]. Such information supports the biodegradable zinc idea and its usability in the bone healing process. The value of recommended daily allowance is ranged between 8-18 mg/day and the excess of the metal can cause problems with the copper deficiency [3, 21, 22].

Limitations of zinc are connected with the mechanical properties and lower value of recommended daily allowance [23]. It can be seen from **Tab. 1**, that the mechanical properties of pure zinc are worse compared with metal used for the implants preparation. The problem is often solved by adding elements or compounds into pure zinc and by a suitable manner of processing. The added components are often those which normally occur in the human body as essential elements (e.g. Mg, Ca, Sr) [24-26] or compounds (e.g. hydroxyapatite, collagen) [27, 28]. Another advantage of adding those components is the possibility of corrosion rate setting, according to conditions that are needed. The setting is connected especially with the exposed surface of the metal (**Fig. 2b**) and galvanic cells formation (**Fig. 2d**). More precisely, the adding of the components leads to decreasing of the specific surface thus decreasing of corrosion rate as well. On the contrary, the formation of the galvanic cell leads to an increase in the corrosion rate. Those statements are general and can be affected by many parameters (e.g. porosity) (**Fig. 2a, b**).

According to this, it is clear that the manner of material processing plays a significant role in the resulting properties. The zinc-based materials, which were prepared by plasma spraying [33], spark plasma sintering, casting and extrusion processes, are shown in **Fig. 2**. The differences in the structures are visible for the first sight but the crucial parameter is the grain size, in the connection with the mechanical properties. The recrystallization temperature of pure zinc is quite low and the grain size can change in wide ranges according to the conditions of preparation [34]. Together with the poor mechanical performance, it is important to mention some approaches and the grain sizes of resulting structures (**Tab 2**).

Tab. 1 Mechanical properties of individual biodegradable materials [10, 15, 16, 29-32]

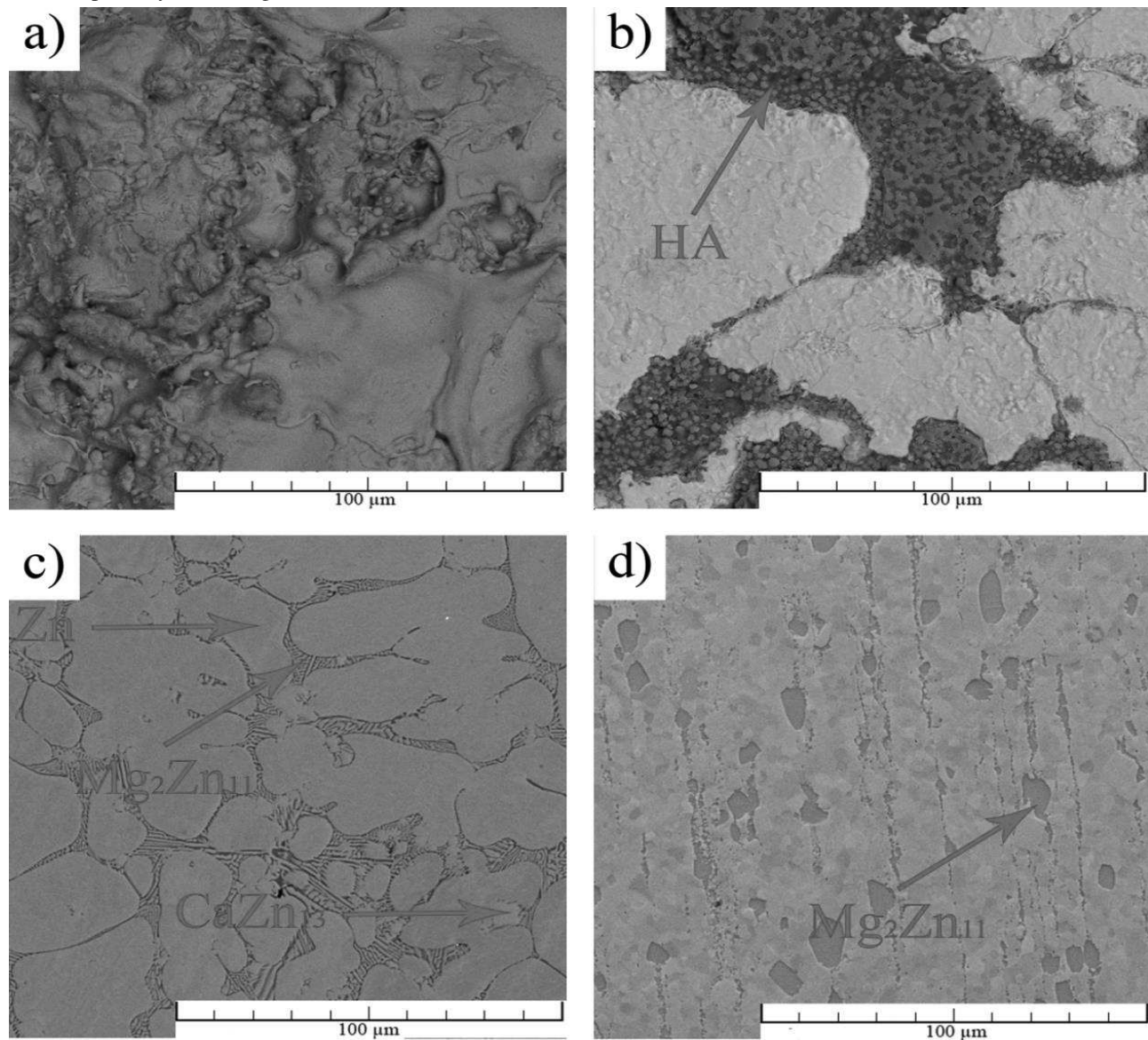
Materials	Young's modulus [GPa]	Ultimate tensile strength [MPa]	Elongation [%]	Hardness
Stainless steel	189–205	490–695	40–52	320–350 HB
Pure Fe	200–205	210–245	40–50	80 HB
Pure Zn	108	88	6	39 HV
Pure Mg	44–45	160	3	30 HB
Magnesium alloy	41–45	65–258	2–13	57–69 HV
Cortical bone	3–30	130–180	–	–
Cancellous bone	0.01 - 1.57	1.5 - 38	–	–

Tab. 2 The grain sizes of zinc prepared by different approaches

Manner of processing	Grain size [μm]
Plasma spraying	1–50
Spark plasma sintering	1–30
Extrusion	5–20

Last but not least, the porosity belongs to the group of significant conditions for the bone implants. It is obvious, that the porosity of biodegradable materials affects the

corrosion properties due to the increase of the surface. This fact can be a little bit problematic in case of biodegradable zinc materials. The reason is that the higher porosity can increase the corrosion rate above the ideal value. Secondly, this increase can lead to premature failure due to the presence of defects and changes in dimensions caused by the corrosion process. The information suggests that the zinc-based biodegradable materials should be non-porous, until the problem with the mechanical properties will be solved.

**Fig. 2** SEM images of zinc-based materials prepared by a) plasma spraying b) spark plasma sintering c) casting d) extrusion

5 Conclusion

In this brief overview of all metals, which are studied as a potentially biodegradable were discussed predominantly from the view of corrosion. Special attention was paid to zinc-based materials. Those materials are the newest from the mentioned metals (Mg, Fe, Zn) and show potential as a material for the biodegradable implant preparation. Despite the disadvantages of zinc connected especially with the mechanical properties, the corrosion properties are almost ideal. The corrosion properties are the most important which is obvious from the intended application. Due to that, the zinc seems to be the ideal material for such application, and it is necessary to solve the problems related to structure in order to use those materials in the human body without negative reactions.

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