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COMPARATIVE MECHANICAL AND CORROSION STUDIES ON MAGNESIUM, ZINC AND IRON ALLOYS AS BIODEGRADABLE METALS

PRIMERJALNA ŠTUDIJA MEHANSKIH IN KOROZIJSKIH LASTNOSTI BIORAZGRADLJIVIH ZLITIN MAGNEZIJA, CINKA IN ŽELEZA

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In this paper, selected magnesium, zinc and iron biodegradable alloys were studied as prospective biomaterials for temporary medical implants like stents and fixation devices for fractured bones. Mechanical properties of the alloys were characterized with hardness and tensile tests. In-vitro corrosion behavior was studied using immersion tests in a simulated physiological solution (SPS, 9 g/L NaCl) to roughly estimate the in-vivo biodegradation rates of implants. It was found that the Mg and Zn alloys were limited by a tensile strength of 370 MPa, while the tensile strength of the Fe alloys achieved 530 MPa. The main advantage of the Mg alloys is that their Young's modulus of elasticity is similar to that of the human bone. However, the corrosion tests revealed that the Mg-based alloys showed the highest corrosion rates in the SPS, ranging between 0.6 mm and 4.0 mm per year, which is above the tolerable degradation rates of implants. The corrosion rates of the Zn alloys were between 0.3 mm and 0.6 mm per year and the slowest corrosion rates of approximately 0.2 mm per year were observed for the Fe alloys. The results indicate that all three kinds of alloys meet the mechanical requirements for the load-bearing implants. From the corrosion-behavior point of view, the Zn- and Fe-based "slowly corroding" alloys appear as promising alternatives to the Mg-based alloys.

Keywords: biodegradable metal, magnesium, zinc, iron, mechanical properties, corrosion

Članek obravnava študij izbranih magnezijevih, cinkovih in železovih potencialnih biorazgradljivih zlitin kot obetajočih biomaterialov za začasne medicinske vsadke, kot so opornice in pripomočki za utrjevanje zlomljenih kosti. Mehanske lastnosti zlitin so bile določene z merjenjem trdote in z nateznimi preizkusi. Korozijski preizkusi in vitro so bili izvršeni s pomakanjem v simulirano fiziološko raztopino (SPS, 9 g/L NaCl) za grobo oceno in vivo hitrosti biorazgradnje implantatov. Ugotovljeno je, da so zlitine Mg in Zn omejene z natezno trdnostjo 370 MPa, medtem ko je natezna trdnost Fe-zlitin dosegla 530 MPa. Glavna prednost Mg-zlitin je v podobnem Young-ovem modulu elastičnosti, ki je podoben kot pri človeški kosti. Vendar pa so korozijski preizkusi pokazali pri zlitinah na osnovi Mg največje korozijske hitrosti v SPS, med 0,6 mm in 4,0 mm na leto, kar je nad dopustno hitrostjo degradacije implantata. Korozijske hitrosti Zn zlitin so bile med 0,3 mm in 0,6 mm na leto, najnižje hitrosti korozije, okrog 0,2 mm na leto, pa so bile opažene pri Fe-zlitinah. Rezultati so pokazali, da vse tri vrste zlitin ustrezajo mehanskim zahtevam za obremenjene implantate. S stališča korozijskega vedenja so zlitine na osnovi Zn in Fe "zlitine s počasno korozijo" in se kažejo kot obetajoče nadomestilo za zlitine na osnovi Mg.

Ključne besede: biorazgradljive kovine, magnezij, cink, železo, mehanske lastnosti, korozija

1 INTRODUCTION

Metallic biomaterials have been used in bone and joint replacements, fractured-bone fixation devices, stents, dental implants, etc., for a long time. The advantage of metals over polymers or ceramics is in higher strength and toughness. In addition, metals can be simply processed with the established technologies like casting, forming, powder metallurgy, machining. The most important metallic biomaterials in the current use are stainless steels (SUS 316L), titanium alloys (Ti, Ti-6Al-4V, Ti-6Al-7Nb), cobalt alloys (Co-Cr-Mo), superelastic Ni-Ti, noble-metal alloys (Au, Pd, dental amalgams – Hg-Ag-Cu-Sn).[1] All these kinds of materials show a high corrosion resistance to human-body fluids due to the noble nature and/or spontaneous passivation and are, therefore, considered as bio-inert materials.[2]

Besides the bio-inert materials, biodegradable materials have attracted a great attention. The term biodegradability means that a material progressively corrodes and degrades in the body environment.[3,4] Products of this degradation are not toxic, allergic or carcinogenic and they are readily excreted by the human body.[3] Biodegradable materials can be used for the implants whose functions in the human body are only temporary, like fixation devices (screws, plates) for fractured bones and stents.[3–5] When using inert biomaterials in bone-fixation devices, a second surgery is often necessary to remove them after the healing process of the bone has completed. In contrast, a biodegradable material slowly degrades in the human body and is progressively replaced by the growing tissue. No second surgery is needed which significantly reduces the inconvenience to the patient, morbidity and health cost. Among the biodegradable materials, polymeric materials (for example poly-lactic acid – PLA) are commonly used at present, but their disadvantages are a low mechanical strength and hardness.[5] For this reason, research and development activities all over the world are also focused on metallic biodegradable alloys with a higher strength, hardness and toughness as compared to the polymers.

Biodegradable alloys should have a good biocompatibility with the human body tissues. This basic requirement limits a number of possible candidates to three metals, magnesium, zinc and iron.[3]

Magnesium is generally considered as a relatively non-toxic metal. It is essential for proper biological functions of the human body. Its recommended daily value is about 400 mg.[6] Magnesium supports the growth of the bone tissue, heart functions, the neurologic system, etc.[7–10] Overdoses of magnesium are unlikely to occur because the metal absorption is efficiently controlled by the metabolism and excess amounts are excreted by the kidneys.[10] There are many studies covering the mechanical, corrosion, in-vitro and in-vivo biocompatibility of the Mg alloys.[11,12] On the basis of these studies, magnesium alloys are generally believed to show a good combination of mechanical performance and biocompatibility depending on the actual alloying elements present. However, the main drawbacks of most of the investigated biodegradable Mg alloys are excessive in-vivo corrosion rates.[4–10]

Iron is also an essential element for proper biological functions, mainly for the transfer of oxygen by blood.[13] The recommended daily value of Fe is about 10 mg.[6] Regarding the biocompatibility of iron-based alloys, there are a number of reported results,[14–16] but they are often controversial. In order to explain the discrepancies between biocompatibility tests, more in-vitro and in-vivo experiments are needed.

Zinc supports the immune system, the proper functions of taste, smell, etc.[11,17] Like Mg, Zn is also a component of many food supplements, therefore, it is considered as relatively non-toxic. Its recommended daily value is about 40 mg, but short-term overdoses of up to 100 mg do not cause significant health problems[18]. Zinc has been considered as a prospective biodegradable implant material only for a relatively short time;[19] therefore, the in-vitro and in-vivo biocompatibility tests with zinc alloys are very limited. However, the tests reported recently indicate a good biocompatibility of Zn.[20]

In the present work, magnesium, zinc, iron and their alloys are studied with respect to their mechanical and corrosion properties. Appropriate alloying of Mg, Zn and Fe can positively modify their mechanical, corrosion and physical properties, which are important for potential medical applications. In the available literature many alloying elements are proposed for these purposes,[3–19] but in this study Mg-RE (RE = rare earth metals, Gd, Nd, Y), Zn-Mg and Fe-Mn based alloys were selected, because all these alloying systems are generally considered as relatively safe and acceptable for a potential medical use.[3]

2 EXPERIMENTS

Chemical compositions of the investigated Mg, Zn and Fe alloys are summarized in **Table 1**. Magnesium and iron alloys were prepared by melting pure metals in a vacuum-induction furnace under argon. Zinc alloys were prepared by melting pure metals in air. The alloys were cast into cast-iron metal molds (Mg, Zn) or sand molds (Fe) to prepare ingots of 20 mm in diameter and 150 mm in length. Parts of the as-cast ingots of Mg and Zn alloys were hot extruded at a temperature of 400 °C, an extrusion ratio of 10 : 1 and a rate of 5 mm/min to prepare rods of 6 mm in diameter. Ingots of iron alloys were hot forged at 850 °C into rods of 6 mm in diameter.

Table 1: Designations and chemical compositions of the studied alloys (w/%)
Tabela 1: Oznake in kemijska sestava preiskovanih zlitin (w/%)

Alloy designation	Element (w/%)						
	Mg	Zn	Fe	Gd	Nd	Y	Mn
Mg	> 99.8	-	0.02	-	-	-	-
Mg-3Gd	bal.	-	0.01	2.7	-	-	-
Mg-3Gd-1Y	bal.	-	0.01	2.6	-	0.8	-
Mg-3Nd-4Y	bal.	-	-	-	2.8	4.2	-
Zn	-	> 99.8	-	-	-	-	-
Zn-1Mg	0.9	bal.	-	-	-	-	-
Zn-2Mg	1.6	bal.	-	-	-	-	-
Fe	-	-	> 99.7	-	-	-	-
Fe-30Mn	-	-	bal.	-	-	-	30.5

The microstructures of the alloys were examined using light (LM) and scanning electron microscopy with energy dispersive spectrometry (SEM + EDS) and X-ray diffraction (XRD). Mechanical properties were characterized with the Vickers-hardness (HV 5) and tensile testing. The tensile tests were carried out on a LabTest 5.250SP1-VM universal loading machine at a deformation rate of 1 mm/min.

In the human body any implant is exposed to fluids containing complicated water solutions of inorganic salts (chlorides, phosphates, etc.), organic compounds (glucose, amino acids, etc.) and biological matter (proteins, cells, etc.). In this study, the biological environment was simulated with a simple NaCl solution, in which the concentration of chlorides is similar to that in the blood plasma. This simulated physiological solution (SPS) contained 9 g/L NaCl, 7×10^{-6} of dissolved oxygen and its initial pH was 6.2 due to dissolved CO_2. The corrosion behavior was characterized with in-vitro immersion tests in the SPS. The alloy samples were immersed in the SPS for 168 h at 37 °C. Afterwards, the corrosion products were chemically removed and the corrosion rates were then calculated, in mm/year, using the weight losses measured with a balance.

3 RESULTS AND DISCUSSION

3.1 Mechanical properties

The Vickers hardness (HV 5), the ultimate tensile strength (*UTS*) and the elongation (*E*) are summarized in **Figure 1**. As expected, pure Mg and Zn show the lowest hardness and strength levels that do not exceed 50 HV 5 and 130 MPa, respectively (**Figures 1a** and **1b**). In contrast, pure iron has higher hardness and tensile-strength values of approximately 100 HV 5 and 300 MPa in the as-forged state. **Figure 1** also demonstrates that both the hardness and the strength of all three groups of alloys increase with the increasing concentrations of the alloying elements due to the solid-solution strengthening and hardening and due to the influence of the intermetallic phases present in the structures. Moreover, positive influences of hot-extrusion or hot-forging operations on the hardness, the strength and the elongation are observed. The reason for the influence is the fact that hot-forming steps cause an elimination of casting defects, dynamic recrystallization and structural refinement, as is illustrated for the Zn-2Mg alloy in **Figure 2**. The as-cast Zn-2Mg alloy (**Figure 2a**) is composed of primary Zn dendrites (light) and an interdendritic network of a Zn + Mg_2Zn_{11} eutectic mixture (dark). A detailed view of the eutectic is seen in the insert in **Figure 2a**. Hot extrusion (**Figure 2b**) partially breaks down the continuous eutectic network and the structure becomes oriented parallel to the extrusion direction. The dynamic recrystallization occurring in the Zn grains (light) results in the formation of equi-axed and refined Zn grains. The average grain size in these regions is 15 μm, which is more than a three-fold reduction in comparison with the primary dendrites in the as-cast alloy (50 μm).

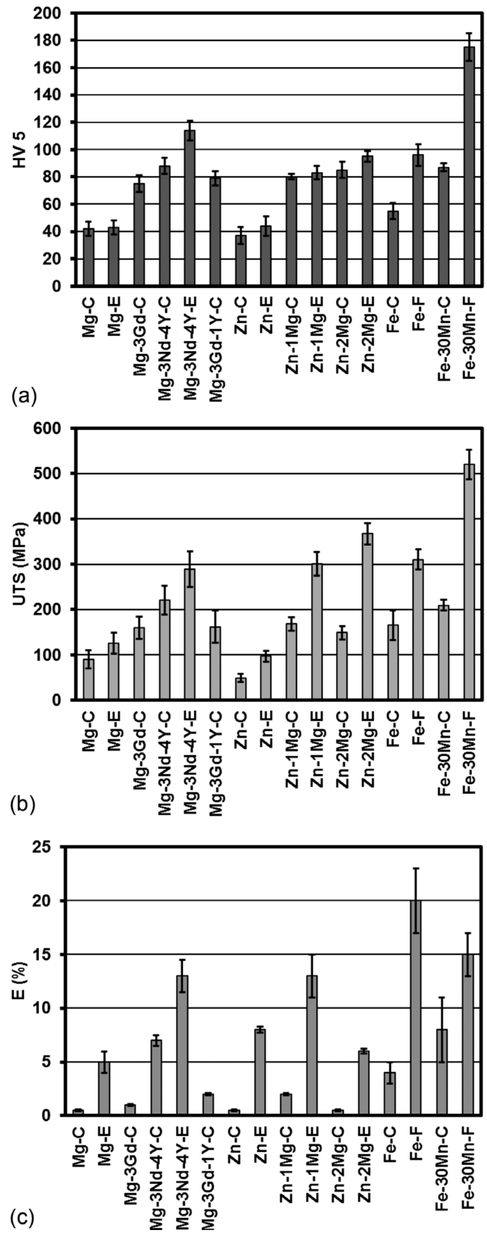

Figure 1: a) Vickers hardness (HV 5), b) ultimate tensile strength (*UTS*) and c) elongation (*E*) of the investigated alloys (C – as cast, E – as hot extruded, F – as hot forged)

Slika 1: a) Trdota po Vickersu (HV 5), b) natezna trdnost (*UTS*) in c) raztezek (*E*) preiskovanih zlitin (C – ulito stanje, E – vroče ekstrudirano, F – vroče kovano)

Figure 1 shows that among the Mg-based alloys, the highest hardness (114 HV 5) and strength (290 MPa) are measured for the hot-extruded Mg-3Nd-4Y alloy due to the presence of the recrystallized and fine-grained structure. This alloy also shows a good elongation of 13 % (**Figure 1c**). Magnesium additions to zinc lead to significant hardening and strengthening of the Zn-Mg alloys. The hot-extruded Zn-2Mg alloy shows the highest hardness (95 HV 5) and tensile strength (367 MPa). But the elongation of this alloy is only 6 %. On the other hand, the Zn-1Mg alloy exhibits a slightly lower tensile strength (301 MPa) but a considerably higher plasticity (elongation of 13 %). As it was expected, the hot-forged Fe-30Mn alloy exhibits the highest hardness (175 HV 5) and strength (530 MPa) among all the studied alloys. The reason is that manganese remains dissolved in γ-Fe, stabilizing the austenitic structure to the room temperature (as proved with XRD) and causing significant solid-solution hardening and strengthening. Moreover, this material also shows an acceptable elongation of 15 %.

It is important to compare the mechanical characteristics of novel biodegradable alloys shown in **Figure 1** with those of today´s commercial biodegradable polymers, for example, the poly-lactic acid (PLA). It is known that the tensile strength of the PLA does not exceed 60 MPa.[1] Therefore, all three groups of metallic biodegradable materials show significantly higher strength levels than the PLA which is of a great importance for load-bearing implants like fixation screws, nails or plates. The advantage of the Mg alloys over the Zn and Fe alloys is a low density (≈ 3 g/cm^3) similar to that of the bone (≈ 2 g/cm^3) and also a low Young´s modulus (≈ 50 GPa). A low modulus is desirable for a proper

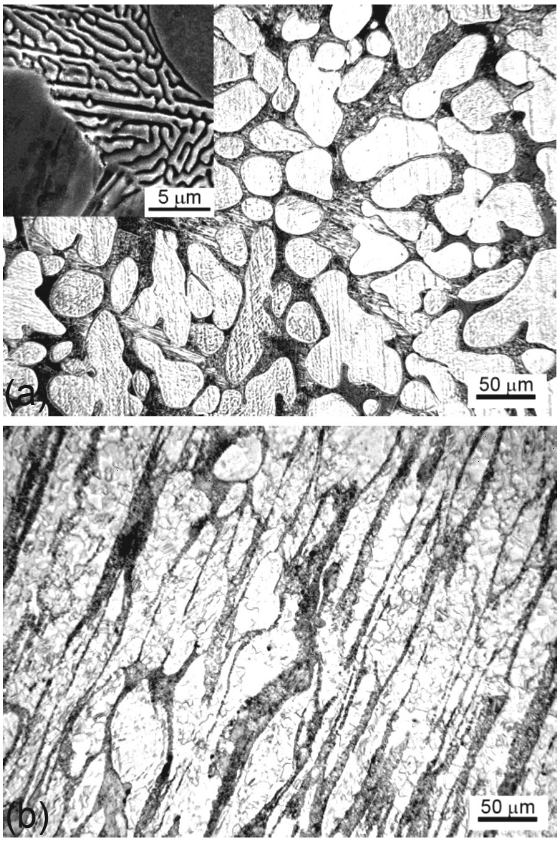

Figure 2: Microstructures of the Zn-2Mg alloy: a) as cast, b) as hot extruded (LM, SEM)

Slika 2: Mikrostruktura Zn-2Mg-zlitine: a) ulito stanje, b) vroče ekstrudirano (SM, SEM)

transfer of mechanical loading between the implant and the bone and for a proper healing process of the bone. The Zn alloys show a strength similar to the Mg alloys but higher density and modulus of elasticity. The Fe alloys are characterized by the highest strength, exhibiting also high density and modulus. As demonstrated in the following section, the advantages of Zn and Fe over Mg are in their lower corrosion rates.

3.2 Corrosion behavior

Figure 3 summarizes the corrosion rates of the alloys in the SPS.

It is observed that, of all the materials, pure Mg corrodes at the highest rate (4 mm per year). The fast corrosion is caused by the presence of impurities, mainly Fe, in magnesium (**Table 1**). It is known that more noble metallic impurities like Fe, Ni, Cu and Co strongly accelerate the corrosion of Mg by forming cathodic sites and micro-galvanic cells with the Mg matrix.[11,12] All the Mg-RE alloys studied show slower corrosion rates in the SPS than Mg. The Mg-3Gd alloy corrodes at the lowest rate (0.6 mm per year). The rare-earth metals reduce the corrosion rate by forming RE-Fe intermetallic phases, which decrease the galvanic effects between the Mg matrix and cathodic impurities. **Figure 3** also indicates that the corrosion rates slightly increase with an increase in the total RE concentration. This may be due to higher volume fractions of the intermetallic phases and the resulting galvanic effects. In comparison with the Mg alloys, the Fe and Zn alloys exhibit significantly lower corrosion rates ranging between 0.2 mm and 0.6 mm per year. The differences between the three groups of alloys are related to different mechanisms of the corrosion process:

Magnesium is the least noble of the three metals studied as its standard potential is –2.4 V (vs. SHE).[2] It thus shows a high tendency to dissolve in water solutions. Magnesium corrosion includes anodic metal dissolution (Equation (1)) and cathodic water decomposition (Equation (2)) to form gaseous hydrogen and to alkalize the solution.[11,12] The corrosion rate of a magnesium implant that is too fast is thus undesirable because both corrosion products have adverse effects on the biocompatibility by negatively influencing the tissue adherence and healing.[21] In the alkaline solutions, surface corrosion products may form, but these products are broken down in the presence of Cl^- anions in the SPS:

$$Mg \rightarrow Mg^{2+} + 2e^- \tag{1}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{2}$$

It is important that the corrosion of the Mg alloys is not controlled by the access of oxidizing species (for example, dissolved oxygen) to the metal. For this reason, it may proceed relatively rapidly even in neutral-water solutions (**Figure 3**). The chloride ions present in the SPS generally accelerate the corrosion process.

Iron is the most noble of all the three metals investigated as its standard potential is –0.4 V (vs. SHE).[2] Therefore, its tendency to dissolve is the lowest. The corrosion process includes anodic dissolution and, in contrast to Mg, cathodic reduction of dissolved oxygen

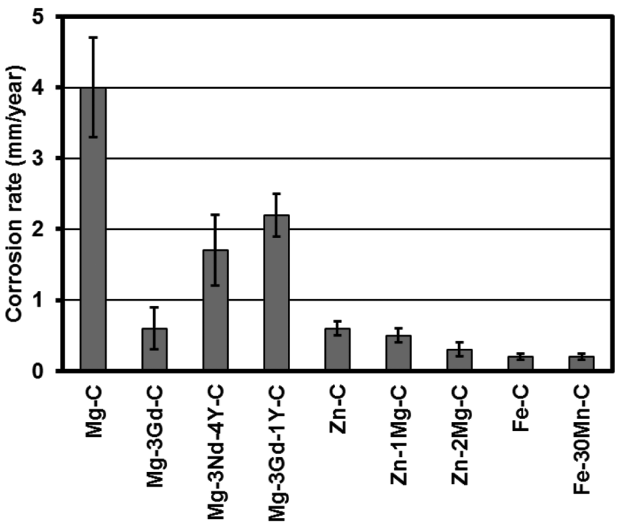

Figure 3: Corrosion rates of the alloys in the SPS measured with immersion tests

Slika 3: Korozijske hitrosti zlitin, potopljenih v SPS

(Equations (3) and (4)). The low corrosion rates of the Fe alloys in the SPS (**Figure 3**) can be attributed to the fact that the corrosion of Fe needs dissolved oxygen whose concentration in the SPS is low. In addition, the corrosion of Fe in neutral solutions is accompanied by the formation of more or less protective corrosion products on the surface. Another positive feature of iron is that its corrosion in neutral solutions does not produce gaseous hydrogen, which would negatively influence the tissue healing around the implant:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (3)$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \quad (4)$$

Zinc nobility is between those of Mg and Fe. The standard potential is –0.8 V (vs. SHE).[2] The corrosion of zinc shows some similarity with iron (Equations (5) and (6)) because it is controlled by dissolved oxygen in the neutral SPS. Therefore, the corrosion process is relatively slow (**Figure 3**). Zinc is also easily covered with protective the passive films of corrosion products in neutral and slightly alkaline solutions. Like in the case of iron, hydrogen gas is not generally formed during the corrosion of zinc in neural solutions. All the above features are good prerequisites for low corrosion rates of zinc implants in human body fluids:

$$Zn \rightarrow Zn^{2+} + 2e^{-} \quad (5)$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \quad (6)$$

Regarding the corrosion process of a biodegradable implant in vivo, it is important to know which corrosion rate is acceptable for a particular application. Too fast an in-vivo degradation of an implant is undesirable because such an implant would degrade before the completion of the healing process. In the case of fixation devices of fractured bones, it is necessary that the implants mechanically fix the bones for a certain minimum period depending on the implant type, design, location, the surrounding tissue, etc. The requirement may be, for example, that a fixation screw must keep 95 % of its original load-bearing capability for at least six weeks after the implantation.[22] In other words, the corrosion of the screw should not reduce its cross-section by more than 5 %, providing the maximum acceptable corrosion rate of 0.4 mm per year. **Figure 3** indicates that the Fe and Zn alloys meet this requirement and that some Mg-RE alloys approach the acceptable corrosion rate. It should be noted that real in-vivo environments contain, in addition to chlorides, like the ones contained by the SPS used in this study, also various organic and inorganic compounds which, in contrast to chlorides, retard the corrosion process by forming protective surface films. For this reason, an in-vivo corrosion would be probably slower than the corrosion in the simple SPS and some Mg-RE alloys would thus also fall into the acceptable range.[23]

4 CONCLUSIONS

In this study, biodegradable Mg, Fe and Zn alloys were compared with regard to mechanical and corrosion properties. It can be concluded that all of these materials show significantly higher strengths than the commercial biodegradable material (PLA). They are thus promising materials for highly loaded implants. In the case of Mg, there are still concerns regarding high corrosion rates, hydrogen-gas release and local alkalization. The main positive feature of the Zn and Fe alloys is their slow corrosion due to the absence of the gaseous-hydrogen release. In addition, the Fe alloys show the highest strength among all the studied materials.

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