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Mechanical properties of magnesium alloys for medical application: A review

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ABSTRACT

Magnesium alloys as a class of biodegradable metals have great potential to be used as implant materials, which attract much attention. In this review, the mechanical properties of magnesium alloys for medical applications are summarized. The methods to improve the mechanical properties of biodegradable magnesium alloys and the mechanical behaviors of Mg alloys in biomedical application are illustrated. Finally the challenges and future development of biodegradable magnesium alloys are presented.

1. Introduction

Biodegradable metals are breaking the current knowledge in biomaterials by the development of corrosion resistant metals. The role of biodegradable implants is to support tissue regeneration, heal the specific trauma and finally disappear through degradation in biological environment. In recent years, biodegradable magnesium (Mg) and its alloys are showing great potential to be used as a new class of materials and are attracting much attention owing to their characteristics of biodegradation (Staiger et al., 2006; Tan et al., 2013; Zhao et al., 2017), anti-inflammatory (Mazur et al., 2007; Peng et al., 2013), antitumor effect (Li et al., 2014a, 2014b; Qu et al., 2013; Wang et al., 2014), antibacterial (Li et al., 2014a, 2014b; Ren et al., 2011; Robinson et al., 2010), osteogenesis inductivity (Chen et al., 2014a, 2014b, 2014c, 2014d; Cheng et al., 2016; Liu et al., 2016; Zhai et al., 2014) and some other biofunctional properties (Guo et al., 2013; Wan et al., 2013; Zeng et al., 2013).

Mg was first reported for medical application in 1878 as ligatures. the physician Edward C. Huse used Mg wires to stop the bleeding vessels of three patients in 1878 (Huse, 1878). He observed that the corrosion of Mg in vivo was slower and the degradation period was dependent on the size of the Mg wire (Huse, 1878). However, pure Mg wire was too brittle to knot easily; therefore some elements were alloyed into Mg to increase its ductility. In 1900, the physician Erwin Payr introduced the idea of using Mg plates and sheets in animal joints to regain or preserve the joint motion. The Mg sheets were implanted in the knee joint of dogs and rabbits, and then the materials completely corroded after 18 days or few weeks, depending on their thickness (Rostock, 1937).

From the end of last century, a new round of study on Mg and its alloys as biodegradable materials has gained much progress. In 2013, the Biotronic Company in Germany obtained the CE mark on a biodegradable Mg alloy's coronary stent and led the development of biodegradable metal coronary stents. In 2013, the Syntellix Co. in Germany obtained the CE mark on a biodegradable Mg alloy's screw after the clinical trial to treat the hallux valgus surgery (Plaass et al., 2016; Windhagen et al., 2013). In December 2016, MAGNEZIX® continued to make its mark: with 25,000 MAGNEZIX® implants, more implants were placed on the market within just 12 months than in the previous 2.5 years. The MAGNEZIX® CBS with 3.5 mm diameter can be used in children, young people and adults as a temporary load-bearing device for bone fixation ("MAGNEZIX® implants"). MAGNEZIX® compression screws have different sizes (MAGNEZIX® CS 2.0, MAGNEZIX® CS 2.7, MAGNEZIX® CS 3.2, MAGNEZIX® CS 4.8) for different treatment (Seitz et al., 2016). Besides, Magmaris (Biotronik AG, Bulach, Switzerland) stent has also received the CE mark in 2016. Magmaris stent is a sirolimus-eluting bioresorbable magnesium scaffold that has better deliverability, radial support and a fast resorption time (Kang et al., 2017). In 2015, the Ministry of Food and Drug Safety of South Korea announced an approval to the K-MET biodegradable metallic screw for osteosynthesis or fixing a broken bone made in U&I Corporation, and 53 cases of hand and wrist fractures fixed by MgCaZn alloy screws were also reported (Lee et al., 2016). Zhao et al. (2016) in China used pure Mg screw for hip-preserving surgery with vascularized bone graft implantation and have finished more than 100 cases of clinical trials. From the clinical applications till present, we can see that the Mg alloy

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screws were mainly used at unload-bearing positions, such as hallux valgus, hand and wrist fractures, and femoral head bone graft fixation. It has been proved (Windhagen et al., 2013) that degradable magnesium-based screws are equivalent to titanium screws for the treatment of mild hallux valgus deformities.

Although the Mg alloy screws in clinic at present are mainly used for unload-bearing positions, they still suffer some mechanical functions, since the function of a surgical bone screw is to clamp together the bone and a bone plate or to fix bone fragments, which is achieved by generation of a tensile stress along the length of the screw, arising from the torsional moment to be introduced into the screw during the implantation process (Hughes and Jordan, 1972). After implantation, the screws need to fix the fracture and suffer the shear strength of the bone, so for the Mg alloy screws, during the degradation in vivo the mechanical fixation is still needed to meet the healing process of the broken bone. Therefore the mechanical property and mechanical integrity of the Mg alloy implants in the physiological environment are of vital importance in effective fracture fixations and cardiovascular surgeries.

The existent permanent metal implants such as titanium alloy, stainless steel and cobalt-chromium alloy in the human body can cause stress shielding because of their higher Young's modulus (Shi et al., 2011). Polymer materials such as poly-L-lactic acid are limited in some clinical applications due to their lower mechanical properties (Chiu et al., 2007). The mechanical properties of Mg alloys compared with some medical materials currently used in clinic are shown in Table 1, in which we can see that the Young's modulus of Mg alloy is much closer to human bone than those of bio-inert medical metals, such as Ti and its alloys, stainless steel and Co-based alloys, however the strength is lower than those of bio-inert metals, but higher than those of biodegradable polymers. This is the reason Mg alloy implants are only applied in unload-bearing position at present, and the mechanical properties of Mg alloys need further improvement to broaden their applications. In this review, the mechanical behaviors and potential medical application of some representative biodegradable magnesium alloys (Mg-Ca based alloys, Mg-Zn based alloys, Mg-Sr based alloys and Mg-RE based alloys…) in a time span of ten years were summarized.

2. Methods to improve the mechanical properties of biodegradable Mg alloys

Magnesium (Mg) is one of the lightest of metals; its alloys have been studied widely. In engineering Mg alloys possessing high specific strength, ductility and creep resistance (Zhu et al., 2015; Yuan et al., 2001). However as a biodegradable material Mg alloys are expected to possess good biocompatibility, high initial mechanical strength and delayed mechanical property decay when implanted in vivo. So for the improvement of mechanical properties of biodegradable Mg alloys, the biocompatibility and degradation properties should also be considered. Requirement to obtain such properties necessitates the alloy development, heat treatment and plastic deformation; all these three aspects are summarized here in this review.

2.1. Alloy development

Alloying is one of the most effective methods to improve the mechanical properties of metals. It has been known that solid solution strengthening and second phase strengthening are the two main ways for improving mechanical properties of magnesium alloys. In addition, to achieve good biocompatibility of the alloys, some nutrient elements have been considered as the first choice to be used as alloying elements, which can form biocompatible Mg alloys and can also improve the strength, which would be different from the engineering designed Mg alloys. Besides, adequate processing has an enormous impact on the mechanical properties of Mg-alloys. For example, heat treatment and plastic deformation. The degradation products have effects on tissue and human metabolism. The corrosion products could promote the bone healing (Witte et al., 2005) and histopathological evaluation of lung, liver, intestine, kidneys, pancreas, and spleen tissue samples showed no abnormalities (Waizy et al., 2014).

Ca is one of the main metal elements in human bone and can improve the bone healing process (Jung et al., 2012; Li et al., 2008; Renkema et al., 2008; Yin et al., 2013). In the Mg-Ca alloy, Mg_2Ca plays a crucial role in the mechanical properties of the alloy with distribution along the grain boundaries (Seong and Kim, 2015a). The addition of Ca to Mg can both increase the strength and the elongation rate due to the grain refinement (Du et al., 2016; Erdmann et al., 2011). However, excessive addition of Ca in magnesium will deteriorate the corrosion resistance. Therefore, Ca concentration in Mg alloys should be less than 1% (Ding et al., 2014). Seong et al. (Seong and Kim, 2015b) revealed that a high volume fraction of Mg_2Ca particles could lead to a deterioration effect on ductility even though they were well refined and dispersed. This was because the interface between Mg and Mg_2Ca was not coherent and the interfacial bonding was weak, thereby easily causing cavities and micro-cracks at the interfaces during plastic deformation. The results showed that the Mg-0.4Ca alloy had the highest tensile ductility (21.9%). However, Zeng et al. (Zeng et al., 2015) found that the Mg-0.79Ca alloy had the highest hardness (58.3 HV) and ultimate tensile strength (~200 MPa) in comparison with the Mg-0.54Ca and Mg-1.35Ca alloys due to the uniform distribution of Mg_2Ca particles.

Zn is one of the important trace elements in human body and a cofactor for optional enzymes in bone and cartilage (Brandão-Neto et al., 1995; Nagata and Lönnerdal, 2011) and Mg-Zn alloys have good biocompatibility (He et al., 2009; Peng et al., 2012; Zhang et al., 2010a, 2010b). Zn has a relatively high solubility in magnesium (6.2 wt%) and can play dual roles in both solid solution and precipitation strengthening (Li et al., 2008; Rosalbino et al., 2013). Zn also can increase age hardening response as it produces intermetallic compounds and refine the grain size (Li and Zheng, 2013; Su et al., 2013). The microstructure of binary as-cast Mg-Zn alloy consists of primary α-Mg matrix and MgZn intermetallic phase distributing along the grain boundary (Kubasek and Vojtech, 2013; Kubasek et al., 2012). It has been proved (Cai et al., 2012) that the strength of Mg-Zn alloy increased with increase of Zn content until 5%. However, the elongation decreased with increase of Zn content. When the content of Zn was over 5%, many MgZn phases would precipitate from Mg matrix along grain boundaries, which could enhance the strength of Mg-Zn alloy due to the dispersion

Table 1
Mechanical properties of medical metals (Chen et al., 2014a, 2014b, 2014c, 2014d; Middleton and Tipton, 2000; Yang et al., 2001).

Metals	Young's modulus (GPa)	Density (g/cm^3)	YS (MPa)	UTS (MPa)	Elongation (%)
Stainless steel(SS316L, annealed plate, ASTM F138)	193	8	190	490	40
Co–Cr alloys (ASTM F90)	210	9.2	310	860	20
Tantalum (annealed)	185	16.6	138	207	–
Pure iron (99.8 wt%)	200	7.87	150	210	40
Mg-based alloy (WE43, ASTM B107/B107M)	44	1.84	170	220	2
DL-PLA	1.9	–	–	27–41	3–10