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Biodegradation and mechanical behavior of an advanced bioceramic-containing Mg matrix composite synthesized through in-situ solid-state oxidation

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ABSTRACT

Recent studies have shown great potential of Mg matrix composites for biodegradable orthopedic devices. However, the poor structural integrity of these composites, which results in excessive localized corrosion and premature mechanical failure, has hindered their widespread applications. In this research, an in-situ Powder Metallurgy (PM) method was used to fabricate a novel biodegradable Mg-bredigite composite and to achieve enhanced chemical interfacial locking between the constituents by triggering a solid-state thermochemical reaction between Mg and bredigite particles. The reaction resulted in a highly densified and integrated microstructure, which prevented corrosion pits from propagating when the composite was immersed in a physiological solution. In addition, chemical interlocking between the constituents prohibited interparticle fracture and subsequent surface delamination during compression testing, enabling the composite to withstand larger plastic deformation before mechanical failure. Furthermore, the composite was proven to be biocompatible and capable of maintaining its ultimate compressive strength in the strength range of cortical bone after 25-day immersion in DMEM. The research provided the necessary information to guide further research towards the development of a next generation of biodegradable Mg matrix composites with enhanced chemical interlocking.

1. Introduction

Magnesium, being among the lightest structural materials, is considered one of the biggest investment opportunities of this century (Luo, 2013). Magnesium is 75% lighter than steel, 50% lighter than titanium, and 33% lighter than aluminum (Kulekci, 2008; NaddafDezfuli et al., 2012). In the biomedical field, particularly in orthopedics, Mg stands out of the rest of the metals in the periodic table due to its biodegradable nature, high strength-to-density ratio and mechanical properties comparable to those of human bone (Witte, 2010).

However, Mg actively dissolves in physiological solutions at an undesirably high rate (NaddafDezfuli et al., 2014), leading to premature structure disintegration and subsequent loss of mechanical properties before the damaged bone is fully recovered. Lowering the degradation rate of Mg has been one of the most studied subjects in pursuit of clinically applicable Mg-based materials (Staiger et al., 2006).

Most of the previous attempts to slow down the biodegradation of Mg were focused on adding alloying elements such as aluminum and zirconium to Mg (Alvarez-Lopez et al., 2010; Hong et al., 2013; Liu et al., 2007), and quite a few, on developing Mg-matrix composites with bioactive particles embedded throughout the Mg matrix (Gu et al., 2010; Witte et al., 2007a; Zheng et al., 2010). Mg matrix composites use monolithic Mg as the metallic matrix so as to avoid possible toxic complications caused by alloying elements (Song, 2007). In addition, the chemical and mechanical properties of Mg matrix composites are adjustable by controlling material parameters such as bioceramic type, particle shape, sizes and distribution as well as processing conditions (NaddafDezfuli et al., 2017b).

In the previous research, Powder Metallurgy (PM) Mg matrix composites containing up to 40 vol% of bredigite were developed and these composites had integrated and homogenous microstructures and mechanical properties similar to those of human bone (NaddafDezfuli et al., 2017a, 2017b). However, the Mg matrix composites still suffered from premature inter-particle fracture and surface delamination under compressive loading (NaddafDezfuli et al., 2017b), causing the outer layer of specimen to be disintegrated from its core, which would be fatal in clinical cases. Inter-particle fracture and surface delamination were identified to be the two dominating failure mechanisms of the Mg matrix composites under mechanical loading, indicating that

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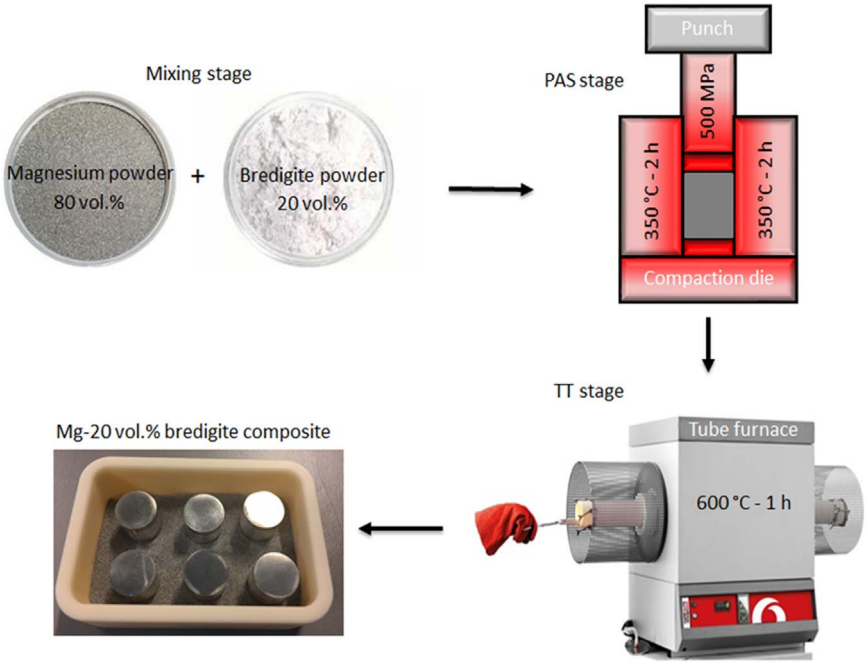

Fig. 1. Schematic illustration of the processing steps for the Mg–bredigite composite.

mechanical interlocking between Mg and bioceramic powder particles was not sufficiently strong to resist inter-particle fracture (NaddafDezfuli et al., 2017b). Inter-particle fracture became even more intense after the composites had been immersed in a physiological solution and suffered from localized corrosion at the edges of specimens. These localized corrosion sites in the Mg-matrix composites would provide nucleation sites for mechanical cracking, thereby reducing their durability if they were used for implants (Witte et al., 2005).

With the recognition of the weak spots in the composites developed earlier, there was a strong desire to improve the composites in terms of structural integrity, degradation behavior and mechanical properties. Improving the integrity of the Mg-bioceramic interface is a challenge because metals generally do not bond strongly with ceramics due to the differences in the nature of atomic bonding in metals and in ceramics (Askeland and Phulé, 2003). Nevertheless, there is a possibility to strengthen the metal-ceramic interface in Mg matrix composites, if an interlayer is formed, which allows chemical interlocking between the constituents. One way to achieve this is to trigger a thermochemical reaction at the Mg-bioceramic interface, causing atoms from both sides to swap by diffusion and forming an intermediate layer as a product of the reaction. The first criterion to achieve this would be the ability of magnesium to reduce oxide phases in bioceramic (e.g., SiO_2) into their elemental constituents (e.g., Si) through a solid state reaction. The second criterion would be the diffusivity of bioceramic elemental constituents into Mg crystal to establish a chemically integrated interface.

With these two criteria in mind, in this research, micro-sized bredigite powder particles was used (bredigite being a biodegradable ceramic in the CaO-MgO-SiO_2 family and known as a bioactive material with mechanical properties close to those of cortical bone and a stimulatory effect on osteoclast proliferation (Wu and Chang, 2007; Yi et al., 2014)), considering the fact that Mg is able to react with bredigite through a solid state oxidation reaction (NaddafDezfuli et al., 2017b), and the possible elemental products of the reaction (such as Si and Ca) are able to diffuse into Mg crystal (Kondoh et al., 2003; Zheng et al., 2010).

The goal of this study was to fabricate biodegradable Mg-bredigite composites with chemical bonding between powder particles, as an additional bonding mechanism to mechanical interlocking to prolong their service life by avoiding premature inter-particle fracture and delamination. Microstructure, mechanical and degradation behavior, in-vitro cytotoxicity and bioactivity of the newly developed composite were evaluated.

2. Materials and methods

2.1. In-situ synthesis of Mg matrix composite

A magnesium powder (containing 320 ppm Fe and 160 ppm Ni impurities – Shanghai Institute of Ceramics) with spherical particles and a mean particle size of 90 μm was mixed with a bredigite ($Ca_7MgSi_4O_{16}$ - Shanghai Institute of Ceramics) powder with a mean particle size of 10 μm and an irregular morphology by 20 vol%. Mixing lasted 12 h using a rotary mixer to obtain a homogenous mixture.

70 mg of the powder mixture was heated from ambient temperature to 620 °C at 2, 5, 10, 15 and 20 °C min^{-1} in a Simultaneous Thermal Analyzer (STA – Setaram SetsysEvo) to pinpoint the critical temperature, at which the thermochemical reaction between Mg and bredigite took place at its highest intensity (T_p), and possible mass change as a result of the exothermic reaction. The STA furnace was flushed with high purity argon gas for 4000 s. The STA tests were repeated three times for each heating rate.

Composite specimens were fabricated using a powder metallurgy method known as Pressure Assisted Sintering (PAS) (NaddafDezfuli et al., 2017b). In this method, the powder mixture was first heated to 350 °C in a 13 mm diameter die made from hot-work tool steel and then uniaxially compacted at 500 MPa. To ensure optimum densification of the PAS composite, the mixture was kept at 350 °C for 2 h under the compaction pressure. The PAS composite was then heated to 600 °C, which was close to the reaction peak temperature measured in the thermoanalytical tests. The thermal treatment was conducted in a tube furnace by heating the PAS composite to 500 °C at a heating rate of 5 °C min^{-1} and then from 500 to 600 °C at 1 °C min^{-1} to exercise more precise control over the heating process. An isothermal step of 1 h was followed, after the composite reached 600 °C, to allow diffusion to take place within and across Mg powder particles. The Thermally Treated (TT) composite was then cooled at 5 °C min^{-1} to room temperature. The thermal treatment was conducted under a protective atmosphere (high-purity argon). An illustration of the processing steps is given in