Acta Biomaterialia 8 (2012) 2375–2383

Contents lists available at SciVerse ScienceDirect

Acta Biomaterialia

journal homepage: www.elsevier.com/locate/actabiomat

Ca–Mg–Zn bulk metallic glasses as bioresorbable metals

J.D. Cao [a,*], N.T. Kirkland [b], K.J. Laws [a], N. Birbilis [b], M. Ferry [a]

[a] School of Materials Science and Engineering, University of New South Wales, NSW 2052, Australia
[b] Department of Materials Engineering, Monash University, VIC 3800, Australia

ARTICLE INFO

Article history:
Received 7 October 2011
Received in revised form 24 February 2012
Accepted 2 March 2012
Available online 9 March 2012

Keywords:
CaMgZn
Bioresorbable metal
Bulk metallic glass
Corrosion
In vitro

ABSTRACT

A series of six unique Ca-based bulk metallic glasses were synthesized and characterized. The glasses were designed to consist solely of the biocompatible elements Ca, Mg and Zn, with the view to their potential use as bioresorbable metals for orthopaedic applications. The alloys had a critical casting thickness of up to 4.5 mm. Mechanical and thermophysical testing revealed a Young's modulus (stiffness) of ~40 GPa. Glass transition temperatures ranged from 119 to 129 °C, above which the alloys can be formed like a thermoplastic polymer. In vitro biocorrosion testing using a combination of polarization and mass loss techniques revealed that the corrosion rate of these alloys is relatively rapid, although, in some cases, it may be tailored through alloy composition.

1. Introduction

In the context of metallic implants, recent years have seen significant attention focused on magnesium and its alloys for use as bioresorbable orthopaedic fixation devices. The majority of studies have tested commercially available grades of crystalline alloys, which were not designed for in vivo use. Recent research has revealed that it is now possible to synthesize bulk metallic glasses (BMG) entirely from Mg, Zn and Ca constituents [1–4], which are elements pre-existing in the body. As a frozen supercooled liquid (SCL), BMG compositions are not limited by the interstitial solubility limit of the elements in the matrix, and therefore a wide range of alloy compositions can be synthesized. The amorphous nature of such BMG and their ability to achieve compositions unattainable by traditional crystalline processing routes may potentially allow for superior corrosion resistance and mechanical properties, with the ability to be shaped like a thermoplastic polymer.

Current bio-inert metallic implant materials such as stainless steel, titanium and cobalt–chromium-based alloys contain elements that are toxic to the human body. Furthermore, the possible release of debris as a result of corrosion or wear is also of significant concern [5–9]. The human body has an inherent tolerance to Mg, Zn and Ca. The adult daily recommended allowances for these elements are 1000 mg day^{-1} Ca [10], 420 mg day^{-1} Mg [11] and 10 mg day^{-1} Zn [12]. In addition, the presence of these ions has been associated with anti-bacterial actions against *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and oral anaerobes [13,14].

Among the bioresorbable Mg-based alloys reported, the most notable is the amorphous Mg-BMG based upon Mg–Zn–Ca. Extract and direct contact cytotoxicity tests using L929 murine fibroblasts and MG63 human osteosarcoma cells have shown improved cell viabilities compared with pure Mg [15]. Furthermore, in vivo assessment in the abdomen of domestic pigs revealed no significant hydrogen evolution [16]. Early attempts, in the first half of the 20th century, to use crystalline Mg as a biomaterial were abandoned owing to hydrogen evolution, which resulted in the formation of subcutaneous gas bubbles [5,17]. The combination of biocompatible elements, immunity to intergranular corrosion and reduced hydrogen evolution makes Mg-BMG a potentially superior implant material to crystalline Mg alloys. However, the glass-forming ability (GFA) of Mg–Zn–Ca BMG is poor, with a critical casting thickness of only ~3 mm reported for $Mg_{66}Zn_{30}Ca_4$ and $Mg_{67}Zn_{28}Ca_5$ (at.%) [1,16]. In addition, the thermoplastic forming (TPF) window of these alloys is only 20 °C. At 135 °C, which is 10 °C below the first crystallization reaction, there is only ~160 s of processing time available before the onset of crystallization.

The ability of BMG to be net-shaped by TPF techniques is one of the biggest advantages of these emerging materials. TPF can only be carried out in the temperature window above the glass transition and below first crystallization. The large SCL region of BMG is useful, since there is a significant decrease in viscosity with increasing deformation temperature that allows these materials to be plastically deformed to very large strains [18,19]. As a result,

* Corresponding author. Tel.: +61 2 9385 5120; fax: +61 2 9385 5956.
E-mail address: cao.jake@gmail.com (J.D. Cao).

1742-7061/$ - see front matter © 2012 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.actbio.2012.03.009