Materials Science & Engineering B 230 (2018) 20–23

Contents lists available at ScienceDirect

Materials Science & Engineering B

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

First principles study of the elastic properties of magnesium and iron based bio-resorbable alloys

Oleg I. Velikokhatnyi[a,d,*], Prashant N. Kumta[a,b,c,d,*]

[a] Department of Bioengineering, University of Pittsburgh, Pittsburgh, PA 15261, United States
[b] Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261, United States
[c] Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA 15261, United States
[d] Center for Complex Engineered Multifunctional Materials, University of Pittsburgh, Pittsburgh, PA 15261, United States

ARTICLE INFO

Keywords:
Bio-resorbable Mg-alloys and Fe-alloys
Density functional theory
Elastic properties
Ductility

ABSTRACT

In the present study, the Density Functional Theory (DFT) implemented in the VASP package has been used to investigate the effects of alloying of different elements deemed biocompatible (Ca, Zn, Li, Zr, Y, Sr, Mn, Ag, RE) when introduced into the Mg and Fe crystal lattice. In particular, the study has been conducted to investigate the general elastic properties, such as bulk modulus, shear modulus, Young's modulus and Poisson's ratio of various Mg- and Fe-based alloys, the results serving to identify candidate bio-resorbable materials potentially suitable for cardiovascular, bronchotracheal, orthopedic and craniofacial applications.

1. Introduction

Bio-inert metals (stainless steels, Ti and Co-Cr-based alloys), biodegradable polymers and bioresorbable ceramics are currently being explored as scaffolds and implants for tissue engineering and regenerative therapies. Metals are more suitable for load-bearing applications due to the combined properties of strength and toughness. However, currently used metallic biomaterials are essentially non-biodegradable, neutral and considered inert *in vivo*, remaining as permanent implants exhibiting no degradable, absorbable or resorption characteristics. As a result, in the case of plates, screws and pins used to secure serious fractures there is inevitably a need for secondary invasive surgical procedure after sufficient healing to remove the implanted fixation devices [1]. Numerous studies (see review [2] and ibid.) have shown the promise of magnesium Mg-alloys as a new class of biodegradable metals for use in stents as well as for craniofacial and orthopedic applications. Magnesium is an exceptionally lightweight metal and has a higher fracture toughness than hitherto used popular ceramic biomaterials such as hydroxyapatite, while its elastic modulus and compressive yield strength are closer to those of natural bone than other commonly used metallic implants.

The desirable low corrosion resistance of Mg, especially in electrolytic and aqueous environments makes it useful for biomaterial applications, wherein the *in vivo* corrosion of the Mg-based implant involves the formation of a soluble, non-toxic hydroxide that is harmlessly excreted in the urine. Magnesium can remain in the body and maintains mechanical integrity over a time scale of 12–18 weeks while the bone tissue heals, eventually being replaced by natural tissue [3].

Magnesium though receiving widespread attention suffers from an undesirable limitation in that pure Mg tends to corrode too rapidly in the physiological system especially with high chloride content releasing hydrogen gas that can cause tissue necrosis and apoptic response in cells. To mitigate this problem various approaches (experimental and theoretical) have been utilized to stabilize the corrosion reaction of the Mg-alloys and also control the eventual release of hydrogen [4–7].

Iron-based alloys are an alternative to Mg-based bio-resorbable alloys if they demonstrate increased corrosion rate compared to pure iron or other industrially used Fe-based alloys when exposed to physiological fluid conditions. These iron based alloys known to date, tend to degrade too slowly, and thus, several studies have been focused on increasing the degradation rates. An iron-manganese binary composition was initially introduced as a biodegradable Fe-based alloy with enhanced corrosion rate and reduced ferromagnetic properties [8]. However, recent literature reports suggest that achieving higher degradation rates in the Fe-Mn alloy system still remains a major challenge and indeed poses a primary limitation preventing the development of biodegradable Fe based alloys for medical device applications [9,10]. For example, in the study [10] elements that are known to exhibit higher aqueous corrosion such as Ca and Mg, well-known for their reactivity in aqueous environments were correspondingly introduced into Fe-Mn alloys to induce higher corrosion of these alloys. As a result, scaffolds of these alloys fabricated using conventional as well as 3-D

* Corresponding authors at: Department of Bioengineering, University of Pittsburgh, Pittsburgh, PA 15261, United States.
E-mail addresses: olv3@pitt.edu (O.I. Velikokhatnyi), pkumta@pitt.edu (P.N. Kumta).

https://doi.org/10.1016/j.mseb.2017.12.024
Received 8 October 2017; Received in revised form 5 December 2017; Accepted 21 December 2017

printing approaches result in faster degradation compared to the Fe-Mn matrix as convincingly demonstrated by D. Hong et al. [10].

Although, a large amount of different prospective bio-resorbable Mg- and Fe-based alloys demonstrating appropriate corrosion behavior for bio-applications have been suggested, an aspect that requires keen attention is the influence of the various alloying elements on specific mechanical properties particularly, modulus, strength and ductility. Theoretical determination and experimental validation of the elastic moduli, Poisson's ratio and ductility characteristics will bode to be extremely useful especially when designing these alloys for *in vitro* and *in vivo* experimental studies. Knowledge of such mechanical properties are very important for the bio-resorbable materials in general, and for cardiovascular as well as bronchotracheal stent applications in particular, since the materials being embedded into the blood vessel must be resilient to the several expansion–contraction cycles arising from the blood flow and air flow related pressures subjected to the stent during the lifetime of the implanted stent device. There is therefore, clearly a need for bioresorbable alloys exhibiting high ductility. Consequently, the search for effective alloying elements to improve the ductility of the Mg- and Fe-based alloys will be extremely useful and is strongly encouraged. For these purposes *ab initio* theoretical approaches will be very useful since they obviate the need for expensive and time consuming trial-and-error experimental procedures involving fabrication of alloys combined with tedious mechanical property measurements of several samples being conducted to obtain statistically meaningful and relevant data before implementation in actual *in vivo* applications.

Based on previously reported theoretical and experimental studies [4–7], a list of select binary and ternary Mg- and Fe-alloys has been created and is shown in Table 1. Bulk (B), shear (G), Young's (E) moduli and Poisson ratio (ν) together with B/G ratio qualitatively reflecting the ductility of the materials (see, for example, S. Pugh [11]) have also been summarized in Table 1. All the Mg-based alloys selected are random solid solutions with hexagonal close packed structure, while the Fe-based alloys adopt cubic symmetry of the crystal lattice.

2. Computational methodology and details

In the present study all the elastic constants were determined from the calculated stresses σ_{ij} associated with strains ε_{kl} applied to hydrostatically equilibrated supercells. Using the stress-strain method where the crystal lattice undertakes a series of different normal and shear deformations determined from a relation between the lattice vectors before and after the transformation, such as $Q' = Q(\varepsilon_{kl})$, one can obtain the respective elastic stiffnesses C_{ijkl} based on the calculated stresses σ_{ij} resulting from such deformations and the corresponding Hook's law $\sigma_{ij} = C_{ijkl}\varepsilon_{kl}$.

Five independent elastic stiffnesses should be calculated for the *hcp* crystal structure: c_{11}, c_{12}, c_{13}, c_{33}, and c_{44}, while only three independent stiffnesses c_{11}, c_{12}, and c_{44} will be calculated for the cubic lattice.

Since, in practice all measurements are obtained for polycrystalline materials, the shear modulus G could be approximately estimated from the elastic constants of the single crystals through the Voigt's approximations for maximum values of the moduli:

$$G = (C_{11} - C_{12} + 3C_{44})/5$$

Considering that the bulk modulus, B is identical for single- and poly-crystalline systems given by:

$$B = (C_{11} + 2C_{12})/3;$$

we can further evaluate the polycrystalline-averaged Young's modulus E and Poisson's ratio ν as follows:

$$E = 9BG/(G + 3B);$$

$$\nu = (3B - 2G)/[2(3B + G)] = (3B - E)/6B;$$

wherein

$$C_{11} = (2c_{11} + c_{33})/3$$
$$C_{12} = (c_{12} + 2c_{13})/3$$
$$C_{44} = (2c_{44} + [c_{11} - c_{12}]/2)/3$$

In the present study for calculation of stresses, the Vienna *Ab-initio*

Table 1
Calculated elastic stiffnesses c_{ij} and different moduli for Mg- and Fe-based alloys (in GPa). Experimental data for Mg in parenthesis are from [16].

Alloy	c_{11}	c_{12}	c_{13}	c_{33}	c_{44}	C_{11}	C_{12}	C_{44}	B *Bulk*	G *Shear*	E *Young's*	ν *Poison's ratio*	B/G
Mg	62.4 (59.5)	23.5 (25.9)	22.0 (21.8)	58.9 (61.6)	16.3 (16.4)	61.2 (60.2)	22.5 (23.2)	17.3 (16.5)	35.4 (35.6)	18.1 (17.3)	46.5 (44.7)	0.28 (0.29)	1.96 (2.06)
Mg-$Zn_{0.03}$	50.9	27.1	25.4	56.2	13.5	52.7	26.0	13.0	34.9	13.1	35.0	0.33	2.66
Mg-$Ca_{0.03}$	54.8	31.1	24.0	65.5	16.4	58.4	26.4	14.9	37.1	15.4	40.6	0.32	2.41
Mg-$Ag_{0.03}$	52.6	29.3	22.7	62.8	16.5	56.0	24.9	14.9	35.3	15.2	39.9	0.31	2.33
Mg-$Sr_{0.03}$	59.1	28.5	24.1	66.0	16.8	61.4	25.6	16.3	37.5	16.9	44.1	0.31	2.22
Mg-$Zr_{0.03}$	59.5	27.8	22.8	65.2	19.5	61.4	24.5	18.3	36.8	18.4	47.3	0.29	2.0
Mg-$Y_{0.03}$	62.3	27.0	24.9	68.4	21.5	64.3	25.6	20.2	38.5	19.9	50.9	0.28	1.93
Mg-$Ca_{0.03}Zn_{0.03}$	52.4	28.2	24.6	63.5	16.0	56.1	25.8	14.7	35.9	14.9	39.3	0.32	2.41
Mg-$Ca_{0.03}Zn_{0.03}Zr_{0.03}$	56.7	29.4	23.1	64.5	17.9	59.3	25.2	16.5	36.6	16.7	43.5	0.30	2.20
Mg-$Ca_{0.03}Zn_{0.03}Y_{0.03}$	58.2	28.8	23.1	69.0	20.8	61.8	25.0	18.8	37.3	18.6	47.8	0.29	2.0
Mg-$Ca_{0.03}Zn_{0.03}Sr_{0.03}$	57.6	29.5	23.8	54.0	16.5	56.4	25.7	15.7	35.9	15.5	40.9	0.31	2.31
Mg-$Ca_{0.03}Zr_{0.03}Sr_{0.03}$	58.3	27.4	23.3	57.7	19.1	58.1	24.7	17.9	35.8	17.4	44.9	0.29	2.06
Mg-$Zn_{0.03}Zr_{0.03}Sr_{0.03}$	55.9	23.3	23.6	58.6	17.9	56.8	23.5	17.4	34.6	17.1	44.0	0.29	2.02
Mg-$Zn_{0.03}Y_{0.03}$	56.4	27.5	24.8	66.3	17.7	59.7	25.3	16.6	37.0	16.8	43.8	0.30	2.20
Mg-$Zn_{0.03}Ce_{0.03}$	56.2	27.2	25.0	65.9	18.0	59.4	25.9	16.7	37.0	16.7	43.5	0.30	2.22
Mg-$Zn_{0.03}Nd_{0.03}$	55.9	26.8	24.3	66.4	17.6	59.4	25.1	16.6	36.5	16.8	43.7	0.30	2.17
Mg-$Zn_{0.03}Sm_{0.03}$	56.3	27.1	24.7	65.6	17.5	59.4	25.5	16.5	36.8	16.7	43.5	0.30	2.20
Mg-$Li_{0.03}$ (0.8 wt%Li)	57.4 (59.0)	26.2 (25.9)	24.1 (21.7)	58.6 (61.0)	18.9 (16.2)	57.8 (59.7)	24.8 (23.1)	17.8 (16.3)	35.8 (35.3)	17.3 (17.1)	44.7 (44.2)	0.29 (0.29)	2.07 (2.06)
Mg-$Li_{0.08}$ (2.5 wt%Li)	55.2 (57.9)	27.7 (25.3)	25.7 (21.2)	55.8 (59.7)	20.6 (15.8)	55.4 (58.5)	26.4 (22.6)	18.3 (16.0)	36.1 (34.6)	16.8 (16.8)	43.6 (43.4)	0.30 (0.29)	2.15 (2.06)
Mg-$Li_{0.17}$ (5.4 wt%Li)	54.1	27.4	26.0	54.4	17.9	54.2	26.5	16.4	35.7	15.4	40.4	0.31	2.32
Mg-$Li_{0.25}$ (8.7 wt%Li)	53.3	26.3	–	–	15.3	53.3	26.3	15.3	35.3	14.6	38.5	0.32	2.41
Mg-$Li_{0.33}$ (12.5 wt%Li)	51.6	24.9	–	–	14.1	51.6	24.9	14.1	33.8	13.8	36.4	0.32	2.45
$Fe_{0.64}Mn_{0.36}$	207	115	–	–	112	207	115	112	145	85.6	214	0.26	1.70
$Fe_{0.61}Mn_{0.36}Ca_{0.03}$	149	120	–	–	100	149	120	100	130	65.8	169	0.28	1.97
$Fe_{0.61}Mn_{0.36}Mg_{0.03}$	200	117	–	–	104	200	117	104	145	79.1	201	0.27	1.83