Available online at www.sciencedirect.com

SciVerse ScienceDirect

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

Research paper

Phase stability, mechanical property, and electronic structure of an Mg–Ca system

*Peng Zhou, H.R. Gong**

State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, China

ARTICLE INFO

Article history:
Received 28 July 2011
Accepted 4 December 2011
Published online 13 December 2011

Keywords:
Biodegradable metals
Magnesium alloys
Computer simulations
Elasticity
Phase transitions

ABSTRACT

First principle calculations reveal that Mg–Ca phases are energetically favorable with negative heats of formation within the entire composition range, and that a strong chemical bonding is formed between Mg and Ca atoms. Calculations also show that the composition has an important effect on mechanical properties of Mg–Ca, and that the Mg–Ca phases with an Mg composition of less than 50 at.% would be good candidates as degradable bone materials in terms of Young's modulus and ductility. In addition, it is found out that Mg_3Ca, MgCa and $MgCa_3$ have phase sequences of BCC → HCP, BCC → HCP and FCC → HCP under high pressure, respectively, and that Ca plays a dominant role in determining the electronic structures and stable crystal structures of various Mg–Ca phases.

1. Introduction

During the past years, magnesium (Mg) alloys have raised great research interests due to their superior properties as biodegradable implant materials, promising to replace the traditional implant candidates such as stainless steel, titanium alloys, ceramics, and polymeric materials, etc. (Witte et al., 2005, 2007; Zhang et al., 2007; Xu et al., 2007; Witte et al., 2008; Staiger et al., 2006; Yao et al., 2009; Zhang et al., 2005; Li et al., 2004; Hort et al., 2010; Hänzi et al., 2009; Gu et al., 2009a; Zhang et al., 2010). It is well known that Mg is an exceptionally light-weighted metal with the density and mechanical properties very close to natural bones, which could benefit the growth of new bone tissues as it minimizes the so-called stress shielding effects which usually happened in the current metallic implants due to the mismatch of their mechanical properties with natural bones (Zhang et al., 2007; Xu et al., 2007; Staiger et al., 2006; Zhang et al., 2005; Li et al., 2004). As an essential element in the human body, Mg shows good biocompatibility as well as no toxicity, and its degradation in human body environment could avoid the second removal surgical operation (Xu et al., 2007). In addition, Mg is relatively abundant in natural resource with low price, and is well regarded to play an important role in human metabolism as well as the properties of human bones (Velikokhatnyi and Kumta, 2010).

The major disadvantage of Mg alloys as biodegradable implant materials is that pure Mg is prone to corrode too quickly at physiological environments and to degrade its mechanical integrity before the tissue has sufficiently healed Staiger et al. (2006). One of the solutions to this problem is the addition of alloying elements such as Al, Ca, Zn, Mn, Li, and Zr, etc., which could also improve the mechanical properties of Mg alloys through solid solution strengthening (Witte et al., 2008). Among these Mg alloys, the binary system of Mg–Ca is regarded as one of the most promising

* *Corresponding author.* Tel.: +86 731 88877387; fax: +86 731 88710855.
E-mail addresses: gonghr@gmail.com, gonghr@csu.edu.cn (H.R. Gong).

1751-6161/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jmbbm.2011.12.001

candidates for biodegradable implant applications, due to the following considerations. First, Mg–Ca alloys would exhibit good biocompatibility and no toxicity, as Ca is a major component in human bones, and also an essential element in human body, just like Mg. This should be a unique quality of Mg–Ca over other Mg alloys, as all elements except Mg and Ca are trace elements in human body and serious problems would appear if their concentrations exceed a certain level (Wan et al., 2008a). Second, another advantage of Mg–Ca is that its density is very close to human bones, as Ca has a low density (1.55 g/cm^3) similar to Mg (1.74 g/cm^3) as well as natural bones (1.8–2.1 g/cm^3) (Li et al., 2008). Third, it is reported that the addition of Ca could improve the corrosion resistance of pure Mg (Velikokhatnyi and Kumta, 2010; Wan et al., 2008a). Fourth, during the degradation of Mg–Ca alloys, the co-releasing of Mg and Ca ions would be beneficial to the healing of human bones (Li et al., 2008).

Regarding the Mg–Ca system, there are already a lot of research papers available in the literature (Velikokhatnyi and Kumta, 2010; Wan et al., 2008a; Li et al., 2008; Krause et al., 2010; Gu et al., 2009a; Zheng et al., 2010; Aljarrah and Medraj, 2008; Gu et al., 2011; Liu et al., 2010; Mishra et al., 2002; Sealy and Guo, 2010; Wan et al., 2008b; Zhou et al., 2008; Kim et al., 2008; Nie and Muddle, 1997; Ortega and Río, 2005; Terada et al., 2011; Ganeshan et al., 2009a,b; Yu et al., 2009; Zhong et al., 2006; Zhang et al., 2009; Sumer and Smith, 1962). To summarize, the experimental studies of Mg–Ca are mainly focused on the alloys compositions with only a very small percentage of Ca (0.6 ∼ 2 wt%) (Li et al., 2008; Gu et al., 2009b, 2011; Liu et al., 2010; Wan et al., 2008b; Kim et al., 2008; Nie and Muddle, 1997; Ortega and Río, 2005), and the theoretical investigations are principally concentrated on the intermetallic phase of Mg_2Ca (Ganeshan et al., 2009a,a; Yu et al., 2009; Zhong et al., 2006; Zhang et al., 2009; Sumer and Smith, 1962). It should be pointed out that the properties of current Mg–Ca alloys are not satisfactory as degradable implant materials, e.g., the Mg–0.8Ca alloy has insufficient initial strength (Krause et al., 2010) and some Mg–Ca alloys are very brittle (Li et al., 2008). To search for new qualified Mg–Ca alloys, it is therefore of importance to have a thorough and systematic study of the correlation between various properties and structures of Mg–Ca phases within the entire composition range. In this respect, it is well known that first principles calculation based on density functional theory can predict the electronic structure and related properties of various metal systems to a high accuracy. The present study is therefore dedicated to investigate the structural stability, mechanical property, high-pressure phase transition, and electronic structure of the Mg–Ca system through first principles calculation.

2. Calculation methods

The first principles calculation is based on the well-established Vienna ab initio simulation package (VASP) within the density functional theory (Kresse and Hafner, 1993). The calculation is conducted in a plane-wave basis, using the projector-augmented wave (PAW) method (Kresse and Joubert, 1999). The exchange and correlation items are described by generalized gradient approximation (GGA) of Perdew et al. (1992) and the cutoff energies are 400 eV for plane-wave basis and augmentation charge, respectively. In each calculation, periodic boundary conditions are added in three directions of the unit cell, and the energy criteria during the relaxation calculation are 0.01 and 0.1 meV for electronic and ionic relaxations, respectively, while the energy criterion is 0.001 meV for the calculation of density of states (DOS) and elastic constants.

At the very beginning, we did a series of test calculation, such as the k-point convergence test. As a result, the k-mesh of 15 × 15 × 15 was adopted for calculation. For k space integration, the temperature smearing method of Methfessel and Paxton (1989) was used for dynamical calculation and the modified tetrahedron method of Blöchl–Jepsen–Andersen (Blöchl et al., 1994) was performed for static calculation.

3. Results and discussion

3.1. Structural stability

In order to find out the ground-state crystal structure of the Mg–Ca system, six compositions, i.e., pure Mg, Mg_3Ca, Mg_2Ca, MgCa, $MgCa_3$ and pure Ca, with several possible ordered structures are selected for total energy calculation. As a typical example, Fig. 1 shows the correlation between the total energy and average atomic volume for the MgCa phase with several structures, respectively. One sees from the figure that the MgCa phase with a $B2$ (BCC lattice) structure has the lowest total energy and is therefore predicted to be the most stable structure corresponding to the ground-state. Similarly, the $A3$ (HCP lattice), $A1$ (FCC lattice), $D0_3$ (BCC lattice), $C14$ (HCP lattice) and $L1_2$ (FCC lattice) are predicted to be the ground-state structures of Mg, Ca, Mg_3Ca, Mg_2Ca and $MgCa_3$ phases, respectively (figures not shown). For convenience, the Bravais lattice symbols (BCC, FCC and HCP), instead of the *Strukturbericht* types, are adopted in the following text, tables, and figures. Accordingly, Table 1 lists the calculated physical properties of these Mg–Ca phases as well as relevant experimental and calculated data in the literature (Yu et al., 2009; Zhong et al., 2006; Zhang et al., 2009; King, 1982, 1981). From Table 1, it is evident that the most stable structures of these Mg–Ca phases predicted from the present calculation match well with available experimental and theoretical observations, and their constants are also consistent with experimental data within an error of less than 2.5%.

To further reveal the structural stability of the Mg–Ca system, the heat of formation of various Mg–Ca phases, ΔH_f, is derived according to the following formula:

$$\Delta H_f = \frac{E_{Mg_mCa_n} - mE_{Mg} - nE_{Ca}}{m+n}, \quad (1)$$

where $E_{Mg_mCa_n}$, E_{Mg} and E_{Ca} are total energies of Mg_mCa_n, pure HCP Mg and FCC Ca, respectively. After the calculation, the derived values of ΔH_f for various Mg–Ca phases are all listed in Table 1. It can be seen from this Table that the most stable structure of each Mg–Ca phase has the lowest ΔH_f,