Intermetallics 95 (2018) 119–129

Contents lists available at ScienceDirect

Intermetallics

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

Atomic cluster structures, phase stability and physicochemical properties of binary Mg-X (X= Ag, Al, Ba, Ca, Gd, Sn, Y and Zn) alloys from *ab-initio* calculations

Jinglian Du[a,b], Ang Zhang[a,b], Zhipeng Guo[a,b,*], Manhong Yang[a,b], Mei Li[c], Shoumei Xiong[a,b,**]

[a] School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
[b] Laboratory for Advanced Materials Processing Technology, Ministry of Education, Tsinghua University, Beijing 100084, China
[c] Materials Research Department, Research and Innovation Center, Ford Motor Company, MD3182, P.O Box 2053, Dearborn, MI 48121, USA

ARTICLE INFO

Keywords:
Mg-based alloys
Atomic cluster structures
Phase stability
Physicochemical property
Ab-initio calculations

ABSTRACT

Both structural and physicochemical properties of binary Mg-X (X = Ag, Al, Ba, Ca, Gd, Sn, Y, Zn) intermetallics were studied by performing *ab-initio* calculations. It was shown that except for Mg-Zn and Mg-Ba alloys, the mass density of the other Mg-X intermetallics changed linearly as the X-content. The local atomic structural features of Mg-X alloys could be well represented by the characteristic principal clusters, which denote the short-range-order structure of the Mg-X alloys. The coordination number (*CN*) of these atomic clusters changed in-between 8 and 16, and most were 12 and 14. The structural stability of Mg-Al, Mg-Ba, Mg-Ag, Mg-Ca, Mg-Sn, Mg-Y and Mg-Gd intermetallics increased as the solute content, while that of Mg-Zn intermetallics decreased as the Zn-content. For each Mg-X alloy system, $MgAl_2$, $MgAg_3$, $Mg_{17}Ba_2$, Mg_2Zn_{11}, MgGd and MgY intermetallics had larger elastic moduli and higher hardness than the others. Besides, $MgAg_3$ and $MgZn_2$ exhibited better plasticity among these Mg-X intermetallics, as reflected by the Poisson ratio and Pugh ratio. All of these Mg-X intermetallics were both thermodynamically and mechanically stable phases, and exhibited conductive metallic features based on the band structures and density of states.

1. Introduction

Magnesium alloys are preferable materials for various lightweight applications including automobile, areoplane and biomedical fields, because of their attractive performances such as high strength-to-weight ratio, good machineability and environmentally friendliness *etc.* [1–6]. These excellent properties primarily originate from the intrinsic microstructures of magnesium alloys, among which the precipitated phases or the so-called intermetallics, together with the primary phase and the impurity segregation, have profound influences on the final performances of the alloy [7–14]. Because of the limited solubility of the additional elements (X) in Mg matrix (induced by chemical affinity differences), stable Mg-containing intermetallic particles or Mg-X precipitates will form during solidification, which significantly influence the microstructure patterns and subsequent mechanical properties of the magnesium alloys [15–19].

Extensive studies have been performed to investigate the intermetallics in different Mg-based alloy systems. Lunder et al. [20] investigated the role of $Mg_{17}Al_{12}$ phase on the corrosion behavior of the AZ91 alloy. Hu et al. [21] investigated the thermodynamic properties of the Mg-RE alloys using a modified embedded atom method. Min et al. [22] analyzed the valence electron structures of intermetallics containing calcium in Mg-Al-based alloys. Chuang et al. [23] reported ternary MgAlZn intermetallic alloys with high Vicker's hardness. Subsequently, the stability, elastic constants, and electronic properties of different intermetallics in binary and ternary magnesium alloy systems were studied systematically *via* first-principle calculations [24–31]. Besides, much more attention also focused on the hydrogen storage property of magnesium alloy, which is believed as one of the most promising candidates for environmental-protecting materials [32,33].

Despite much progress on the formation and performances of intermetallics in different Mg-based alloy systems, it is clear that understanding both atomic cluster structures and physicochemical properties is essential for the development of new Mg-based alloys. In this work, the characteristic atomic cluster structures representing short-range-order (SRO) features, as well as thermodynamic, mechanical and electronic properties of binary Mg-X (X = Ag, Al, Ba, Ca, Gd, Sn, Y and Zn) intermetallics were investigated by performing *ab-initio* calculations.

* Corresponding author. School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.
** Corresponding author. School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.
E-mail addresses: zhipeng_guo@mail.tsinghua.edu.cn (Z. Guo), smxiong@tsinghua.edu.cn (S. Xiong).

https://doi.org/10.1016/j.intermet.2018.02.005
Received 23 November 2017; Received in revised form 12 January 2018; Accepted 5 February 2018

Table 1
Crystallographic information and mass density of the Mg-X (X = Ag, Al, Ba, Ca, Gd, Sn, Y, Zn) alloys, together with other reported values.

Phase	Space group	Prototype	Pearson symbol	Unitcell lattice parameter (Å)		Mass density (kg/m^3)	Reference
Mg	$P6_3/mmc$	Mg	$hP2$	a = 3.2094	c = 5.2105	1736.67	This work
				a = 3.2065	c = 5.2256	1747.32	[35]
MgAg	$Pm\bar{3}m$	CsCl	$cP2$	a = 3.3306		5940.04	This work
				a = 3.3302		5942.25	[35]
$MgAg_3$	$Pm\bar{3}m$	$AuCu_3$	$cP3$	a = 4.1609		8019.61	This work
				a = 4.1090		8023.08	[35]
Ag	$Fm\bar{3}m$	Cu	$cF4$	a = 4.0857		10505.2	This work
				a = 4.0863		10500.0	[35]
$Mg_{17}Al_{12}$	$I\bar{4}3m$	Mn	$cI58$	a = 10.5296		2096.46	This work
				a = 10.5438		2085.67	[35]
$MgAl_2$	$I4_1/amd$	Ga_2Hf	$tI24$	a = 4.2004	c = 24.9958	2357.61	This work
				a = 4.1320	c = 26.6020	2368.37	[35]
$Mg_{23}Al_{30}$	$R\bar{3}$	$Co_5Cr_2Mo_3$	$hR53$	a = 12.7663	c = 21.7569	2219.97	This work
				a = 12.8254	c = 21.7478	2220.43	[35]
Al	$Fm\bar{3}m$	Cu	$cF4$	a = 4.0495		2698.85	This work
				a = 4.0500		2697.29	[35]
$Mg_{17}Ba_2$	$R\bar{3}m$	$Zn_{17}Th_2$	$hR19$	a = 10.6179	c = 15.5884	2251.37	This work
				a = 10.4970	c = 15.5170	2224.69	[43]
$Mg_{23}Ba_6$	$Fm\bar{3}m$	$Mn_{23}Th_6$	$cF116$	a = 15.2086		2611.31	This work
				a = 15.2130		2579.63	[43]
				a = 15.220		–	[30]
Mg_2Ba	$P6_3/mmc$	$MgZn_2$	$hP12$	a = 6.6517	c = 10.5851	3044.96	This work
				a = 6.660	c = 10.5640	3500.90	[43]
				a = 6.6650	c = 10.5770	–	[30]
Ba	$Im\bar{3}m$	W	$cI2$	a = 5.0190		3607.39	This work
Mg_2Ca	$P6_3/mmc$	$MgZn_2$	$hP12$	a = 6.2458	c = 10.0763	1730.46	This work
				a = 6.2250	c = 10.1800	1738.68	[35]
				a = 6.2390	c = 10.0990	1716.94	[43]
				a = 6.2340	c = 10.0930	–	[30]
Ca	$Fm\bar{3}m$	Cu	$cF4$	a = 5.5820		1530.62	This work
				a = 5.5884		1532.56	[35]
Mg_2Gd	$Fd\bar{3}m$	Cu_2Mg	$cF24$	a = 8.5571		4364.44	This work
				a = 8.550		4366.09	[35]
Mg_3Gd	$Fm\bar{3}m$	BiF_3	$cF16$	a = 7.3301		3881.70	This work
				a = 7.310		3883.56	[35]
MgGd	$Pm\bar{3}m$	CsCl	$cP2$	a = 3.8043		5474.79	This work
				a = 3.8245		5476.68	[35]
Gd	$P6_3/mmc$	Mg	$hP2$	a = 3.6315	c = 5.7770	7915.26	This work
				a = 3.6330	c = 5.7739	7918.56	[35]
Mg_2Sn	$Fd\bar{3}m$	Cu_2Mg	$cF24$	a = 6.8204		3502.42	This work
				a = 6.7620		3505.67	[35]
				a = 6.8250		–	[30]
Sn	$Fd\bar{3}m$	C	$cF8$	a = 6.4912		5764.72	This work
				a = 6.4892		5765.65	[35]
$Mg_{24}Y_5$	$I\bar{4}3m$	Mn	$cI58$	a = 11.2622		2389.69	This work
				a = 11.2780		2390.58	[35]
				a = 11.260		–	[43]
Mg_2Y	$P6_3/mmc$	$MgZn_2$	$hP12$	a = 6.0496	c = 9.8221	2934.03	This work
				a = 6.0370	c = 9.7520	2936.56	[35]
MgY	$Pm\bar{3}m$	CsCl	$cP2$	a = 3.7954		3438.53	This work
				a = 3.810		3436.89	[35]
				a = 3.8030		–	[30]
Y	$P6_3/mmc$	Mg	$hP2$	a = 3.6451	c = 5.7305	4477.84	This work
				a = 3.6475	c = 5.7307	4479.23	[35]
Mg_2Zn_{11}	$Pm\bar{3}$	Mg_2Zn_{11}	$cP39$	a = 8.5240		6175.65	This work
				a = 8.5525		6160.98	[35]
$MgZn_2$	$P6_3/mmc$	$MgZn_2$	$hP12$	a = 5.2150	c = 8.4821	5155.64	This work
				a = 5.170	c = 8.50	5156.69	[35]
Zn	$P6_3/mmc$	Mg	$hP2$	a = 2.6649	c = 4.9468	7136.86	This work
				a = 2.6650	c = 4.9470	7138.68	[35]

These additional elements, spanning much of the periodic table, are of great scientifical and technological significance for developing Mg-based alloys with favorable compositions and desired properties [15,16,24,28,34]. In particular, Al and Zn can improve both strength and ductility, Ca can enhance the creep resistance of Mg-Al alloys by replacing the detrimental $Mg_{17}Al_{12}$ phase with more stable Laves phases, Sn can improve the ductility in the bulk forming process, while the rare elements Y and Gd can improve both structure and property. The present investigations will provide great insight into understanding the atomic structures and physicochemical properties of Mg-based alloys.

2. Computational methodology

The crystallographic information of binary Mg-X (X = Ag, Al, Ba, Ca, Gd, Sn, Y and Zn) intermetallics studied in this work were listed in Table 1 [35]. These Mg-X intermetallics included the MgX phase with simple structure, i.e. 2 atoms *per* primitive cell, and the $Mg_{23}X_6$ phase with complicated structure, i.e. 116 atoms *per* primitive cell. All of the theoretical calculations were performed using the Vienne Ab initio