Structural stability and elastic constants of precipitate phases of Mg-5%Al alloy with combined Ca and Sr addition from first-principles calculations

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Abstract. The calculated lattice parameters and enthalpies of formation of Al_2Ca , Al_2Sr , Al_4Ca , Al_4Sr , Mg_2Ca , and Mg_2Sr phase in Mg-Al-Ca-Sr alloy system were compared with both calculation results and experimental data published in references available, and the structural stability of these intermetallic compounds phases were estimated from the energetic point of view. The results showed that Al_2Ca phase had a higher structural stability. After further calculation of lattice parameters and enthalpies of formation of $\text{Al}_2(\text{Ca},\text{Sr})$ phase with Sr and Ca variation respectively, the structural stability of $\text{Al}_2(\text{Ca},\text{Sr})$ phase was predicted from the thermodynamic point of view. The results showed that $\text{Al}_2(\text{Ca},\text{Sr})$ phase had a good alloying ability and the $\text{Al}_2(\text{Ca},\text{Sr})$ with various Ca/Sr atom ratio was either stable, which demonstrated the mutual solubility of Ca and Sr in $\text{Al}_2(\text{Ca},\text{Sr})$ phase. The elastic constants and mechanical parameters for Mg, $\text{Al}_2(\text{Ca},\text{Sr})$ and Al_4Sr in Mg-5%Al-Ca-Sr alloy were further calculated. Results showed that the obtained elastic constants and mechanical parameters of Mg were accordant with the experimental results and Al_4Sr is both of the best ductility and plasticity, while $\text{Al}_2(\text{Ca},\text{Sr})$ is both of poorest ductility and plasticity in Mg-Al-Ca-Sr alloy.

Introduction

As the lightest metal structural materials, magnesium alloys are being used to speed up the process of lightweight in automotive, motorcycle and aerospace field due to their high strength-to-weight ratio, specific strength, stiffness and low density [1]. Moreover, the weight reduction of engineering parts can bring on reduced energy consumption and beneficial environmental implications. As to the problem that the creep resistance will reduce at elevated temperature (above around 398K) of Mg-Al alloys, the ideal that to introduce intermetallic compounds with high melting point through addition of alloying elements was thus of interest. RE addition to Mg-Al alloys was proven to solve the problem initially [2-4]. And the low cost alkaline-earth elements with smaller density, especially the combined Ca and Sr addition, were chosen to try to replace RE additions [5-8]. Therefore, it was necessary to focus on the properties of the introduced intermetallic compounds. There has been some works on the electronic structures and stabilities of intermetallic compounds in Mg-Al-Ca system [9-11]. And for Mg-Al-Ca-Sr system, there are only reports about thermodynamic properties and phase diagrams [12-14]. Up to now, the reports for the properties of the intermetallic compounds in Mg-Al-Ca-Sr system, such as the electronic structures, stabilities and the elastic constants are very limited, either experimentally and theoretically. Generally, elastic properties of a precipitate phase are of importance because the anisotropy and mechanical properties such as the bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (B/G) can be calculated from elastic constants, so they are useful information when considering the effects of the secondary phases on the based materials.

As for the commercial magnesium alloys, such as AZ31, AZ61, AZ91, the content of Al was less than 9wt.% due to the solubility of element Al in Mg matrix. Therefore, in this work, the Mg-5wt.% Al based alloy system with combined Ca and Sr addition was chosen to study. A. Janz and R. Schmid-Fetzer[17] revealed the ternary solubility of Sr in the binary Al_2Ca phase experimentally. And up to now, the theoretical investigations on the elastic properties and stability of $\text{Al}_2(\text{Ca}, \text{Sr})$ are scarce.

In the present work, the lattice parameters and enthalpies of formation of end-member binary phases (Al_2Ca , Al_2Sr , Al_4Ca , Al_4Sr , Mg_2Ca , and Mg_2Sr) in Mg-Al-Ca-Sr alloy system were compared with both calculation results and experimental data published in references available, and the alloying ability of these intermetallic compounds phases were estimated from the energetic point of view. Furthermore, structural, elastic properties of $\text{Al}_2(\text{Ca}, \text{Sr})$, Al_4Sr and matrix Mg were calculated. And the exhibited form of Ca and Sr in Mg-Al based alloys was analyzed. The ductility, plasticity and elastic anisotropy of the secondary phases were further discussed and compared with that of the matrix Mg. This work aimed at the solid solubility of alloying elements in the secondary phase in magnesium alloys theoretically, and tried to explore a new insight to the secondary phase strengthening magnesium alloys.

Computational method and model

Here in this work, all the first-principles calculations, which was based on density functional theory (DFT)[19], were carried out using the generalized gradient approximation refined by Perdew, Burke and Ernzerhof (PBE) [20] as implemented in VASP (Vienna Ab-initio Simulation Package) code [21-22]. The projector augmented wave method (PAW) [23] was employed to described the ion – electron interaction .

Fig. 1. The crystal structure of Al_2Ca . The red spheres were Al atom and blue ones were Ca atom. a-a', b-b', c-c' and d-d' indicated the equivalent point positions of atoms for Ca.

The cut-off energy of plane wave was set at 360 eV for $\text{Al}_2(\text{Ca}, \text{Sr})$ with various Sr solubility, Al_4Sr and matrix Mg. The Brillouin zone integration used Monkhorst-Pack grids of $9 \times 9 \times 9$ mesh for optimizing geometry and calculating elastic constants, and $12 \times 12 \times 12$ for calculation of the enthalpies of formation and the density of states (DOS). Extensive tests of k-point indicated that the total energy differences converged to within 0.001 eV/atom. The geometry optimization was carried out by full relaxation until the total energy changes within 10^{-5} eV/atom and the Hellmann-Feynman force on all atoms was less than 10^{-2} eV/Å. In order to study the effect of solid-soluted Sr on the properties of $\text{Al}_2(\text{Ca}, \text{Sr})$ phase, the crystal models of $\text{Al}_2(\text{Ca}_{0.875}, \text{Sr}_{0.125})$, $\text{Al}_2(\text{Ca}_{0.75}, \text{Sr}_{0.25})$, $\text{Al}_2(\text{Ca}_{0.625}, \text{Sr}_{0.375})$ with various Sr solubility were built with substitutions of 1 Sr atom for Ca in position of a, 2 Sr for Ca in positions of a and b', 3 Sr for Ca in positions of a, b

and a' respectively. The atom positions of a-a', b-b', c-c' and d-d' were shown in Fig.1. All the substitute atom position or the combined atom positions were determined according to the minimum total energy after careful test.

Results and discussion

Crystal structure and alloying ability

In order to study the alloying ability of the end-member intermetallic compounds in Mg-Al-Ca-Sr alloy system and try to predict the possible phases in Mg-5%Al alloy with combined Ca and Sr addition, the enthalpies of formation of Al₂Ca, Al₂Sr, Al₄Ca, Al₄Sr, Mg₂Ca and Mg₂Sr were calculated and compared with the available experimental values in references, as shown in Table 1.

Table1 Equilibrium lattice constants (a, c) and enthalpy of formation (ΔH) of pure constituents and intermetallic compounds

intermetallic compounds	Lattice constant(/nm)				Enthalpy of formation (eV.atom-1)	
	Cal.	Exp.		Cal.	Ref.	
		a	c			
Mg	0.321	0.5148	0.3209	0.5203	-1.4745	
Al	0.4052	-	0.4056	-	-3.6925	
Ca	0.5506	-	0.557	-	-1.9134	
Sr	0.6003	-	0.6085	-	-1.624	
Al ₂ Ca	0.8011	-	0.8035	-	-0.359	-0.37 ^a
Al ₂ Sr	0.8283	-	0.8325	-	-0.283	
Al ₄ Sr	0.4467	1.1228	0.445	1.105	-0.2614	
Al ₄ Ca	0.435	1.1225	0.435	1.107	-0.2247	-0.22 ^a
Mg ₂ Ca	0.6224	1.0077	0.6271	1.017	-0.1316	-0.135 ^b
Mg ₂ Sr	0.6457	1.0401	0.6483	1.0451	-0.1164	

^a from Ref.[10]

^b from Ref.[30]

To determine the accuracy of calculation, the calculated lattice constants of pure elements and the compounds were compared with those determined by experiments, as shown in Table 1. It can be seen that the calculated data agreed well with experimental results. The formation enthalpies ΔH (eV.atom⁻¹), which can be defined as the difference in total energy of the compound and the energies of its constituent elements in their stable states:

$$\Delta H(A_x B_y) = \frac{1}{x+y} [E_{total}(A_x B_y) - xE_{total}(A) - yE_{total}(B)] \quad (1)$$

Where $E_{total}(A_x B_y)$ was the total energy of the compound $A_x B_y$, and $E_{total}(A)$ and $E_{total}(B)$ were the energy per atom of pure elements of Mg, Al, Ca and Sr in their ground state. It was necessary to point out that the energies were calculated at 0 K without any entropic contributions, the energy of formation was considered as the enthalpy of formation [24]. It can be found in Table 1 that the calculated energy of formation in this work presented good agreement with the available data in previous calculations[10][30]. Negative value of formation enthalpy indicated an exothermic reaction, so Al₂Ca, Al₂Sr, Al₄Ca, Al₄Sr, Mg₂Ca and Mg₂Sr could be stable. Furthermore, the lower the formation enthalpy was, the stronger the stability and the alloying ability were. The calculated energy of formation of Al₂Ca was -0.359 eV.atom⁻¹, with the minimum negative value, so determination can be made that Al₂Ca phase had a higher structural stability and alloying ability, followed by Al₂Sr, Al₄Sr and Al₄Ca. Therefore, the most possible phases in Mg-5%Al alloy with combined Ca and Sr addition were Al₂Ca and Al₂Sr, if there was enough Al, Al₄Sr and Al₄Ca may be possible to form.

It was reported that the equilibrium constituent phases in $\text{Mg}_{91.63}\text{Al}_{4.97}\text{Ca}_{3.23}\text{Sr}_{0.35}$ (wt. %) alloy were matrix Mg, $\text{Al}_2(\text{Ca},\text{Sr})$ as the predominant secondary phase and Al_4Sr with a few amount, and the $\text{Al}_2(\text{Ca},\text{Sr})$ phase was a binary phase with ternary solubility[18]. This phenomenon was a little bit general on the secondary phase in magnesium alloys [24]. So it can be concluded from the experimental results that Ca and Sr were mainly in form of $\text{Al}_2(\text{Ca},\text{Sr})$ in Mg-5%Al alloy with combined Ca and Sr addition. In order to study the effect of solid-soluted Sr on the structural stability of $\text{Al}_2(\text{Ca},\text{Sr})$ phase, the formation enthalpy of $\text{Al}_2(\text{Ca},\text{Sr})$ phase with various Sr solubility was compared with that of Al_2Sr , as shown in Table 2 and Fig.2.

Table 2 Equilibrium lattice constants and the formation enthalpy (ΔH) of Al_4Sr and $\text{Al}_2(\text{Ca},\text{Sr})$ phase with various Sr solubility

Compounds	Solid solubility of Sr	Displaced position of Sr	Lattice constant a/(nm)	Enthalpy of formation (KJ/mole)
Al_2Ca	0	-	8.035	-34.46
$\text{Al}_2(\text{Ca}_{0.875},\text{Sr}_{0.125})$	0.125	a	8.048	-32.111
$\text{Al}_2(\text{Ca}_{0.75},\text{Sr}_{0.25})$	0.25	ab'	8.084	-29.856
$\text{Al}_2(\text{Ca}_{0.625},\text{Sr}_{0.375})$	0.375	aba'	8.118	-27.657
Al_2Sr	1	-	8.28	-27.16

It can be observed from Table.2 and Fig.2 that the formation enthalpy of the $\text{Al}_2(\text{Ca},\text{Sr})$ phase increased linearly as the solubility of Sr increased. When the solid solubility of Sr increased to 0.375, the formation enthalpy increased to -27.657 KJ/mole, and it is a little bit lower than the that of Al_2Sr . So we can get that the $\text{Al}_2(\text{Ca},\text{Sr})$ phase with solid solubility of Sr up to 37.5at.% was more stable than Al_2Sr . So the Ca and Sr presented in form of $\text{Al}_2(\text{Ca},\text{Sr})$ phase instead of Al_2Ca or Al_2Sr phase. This prediction agree very well with the experimental results in ref [18].

Fig.2. Calculated formation enthalpy of the $\text{Al}_2(\text{Ca},\text{Sr})$ phase with various Sr solubility. A indicated the value of Al_2Sr .

Elastic properties

To evaluate the elastic properties of the matrix Mg and the secondary phases in the alloy system, elastic constants of Mg, $\text{Al}_2(\text{Ca}_{0.75},\text{Sr}_{0.25})$ and Al_4Sr were calculated and compared. For a materials with hexagonal symmetry, there were five independent elastic constants, C_{11} , C_{12} , C_{13} , C_{33} and C_{44} . And for a materials with cubic symmetry, there were only three independent elastic constants, C_{11} , C_{12} and C_{44} . And for a materials with tetragonal symmetry, the independent elastic were C_{11} , C_{12} , C_{13} , C_{33} , C_{44} and C_{66} . Elastic constants can be calculated through applying small strains to the equilibrium unit cell and determining the corresponding variations in the total energy. If we impose stain on the lattice by deforming the primitive vectors, then relax all the internal parameters to minimize the total energy, we may get all the independent C_{ij} . Define a strain tensor $\vec{\epsilon}$, so that the primitive vectors $\vec{a}_i$ were transformed to the new vectors $\vec{a}'_i$.

$$\vec{a}_i' = \begin{pmatrix} \mathbf{a}_1' \\ \mathbf{a}_2' \\ \mathbf{a}_3' \end{pmatrix} = \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} \cdot (\vec{I} + \vec{\varepsilon}) \quad (2)$$

where $\vec{I}$ was the 3×3 identity matrix, $\vec{\varepsilon}$ was the strain tensor given by

$$\vec{\varepsilon} = \begin{bmatrix} e_1 & e_6/2 & e_5/2 \\ e_6/2 & e_2 & e_4/2 \\ e_5/2 & e_4/2 & e_3 \end{bmatrix} \quad (3)$$

The relationship between total energy increment and the elastic constants C_{ij} was as follow:

$$U = \frac{\Delta E}{V_0} = \frac{1}{2} \sum_i \sum_j C_{ij} e_i e_j \quad (4)$$

Where the V_0 was volume of the undeformed lattice, $\Delta E = E_{\text{totl}}(V_0, \delta) - E_{\text{total}}(V_0, 0)$ is the total energy difference between the deformed cell and the initial cell, V_0 is the volume of equilibrium cell and C_{ij} is the elastic constant. δ is the deformation added to the equilibrium cell. For each kind of lattice deformation, the total energy has been calculated for different strains. By means of polynomial fit, we extracted these values of the second-order coefficients, which were corresponding to $3(C_{11} - C_{12})$, $3(C_{11} + 2C_{12})/2$ and $C_{44}/2$ for cubic symmetry and $C_{11} + C_{12}$, $(C_{11} - C_{12})/4$, $C_{33}/2$, C_{44} and $C_{11} + C_{12} + 2C_{13} + C_{33}/2$ for hexagonal symmetry, and $C_{11} + C_{12}$, $C_{11}/2$, $C_{33}/2$, $C_{11} + C_{12} + 2C_{13} + C_{33}/2$, C_{44} and $C_{11} + C_{12} + C_{66}/2$ for tetragonal symmetry, respectively. The elastic constants were obtained, and the results are tabulated in Table 3.

Table 3 The calculated elastic constants (in GPa) of Mg, Al₂ (Ca_{0.75}, Sr_{0.25}) and Al₄Sr

Material	symmetry	Elastic constants					
		C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
Mg	hexagonal	62.620	24.754	20.668	65.502	18.318	-
		59.740 ^c	26.140 ^c	21.670 ^c	72.600 ^c	18.420 ^c	-
Al ₂ (Ca _{0.75} , Sr _{0.25})	cubic	111.631	27.908	-	-	42.054	-
Al ₄ Sr	tetragonal	75.012	44.888	32.417	120.452	7.120	35.020

^c from Ref.[26]

These elastic constants satisfy the generalized elastic stability criteria for cubic crystals[27-28]: $(C_{11} + 2C_{12})/3 > 0$, $C_{11} - C_{12} > 0$ and $C_{44} > 0$, and for hexagonal crystals: $C_{11} > 0$, $C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{33} (C_{11} - C_{12}) - 2C_{13}^2 > 0$ and for hexagonal crystals: $C_{11} > |C_{12}|$, $C_{33} (C_{11} + C_{12}) > 2C_{13}^2$, $C_{44} > 0$, $C_{66} > 0$. These conditions also lead to a restriction on the magnitude of B: $C_{12} < B < C_{11}$. The bulk modulus B, shear modulus G, Young's modulus E and anisotropy value A were deduced according to the following formulae:

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (5)$$

$$G = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad (6)$$

$$E = \frac{9BG}{G + 3B} \quad (7)$$

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (8)$$

Then Poisson's ratio ν was obtained from

$$\nu = \frac{3B - E}{6B} \quad (9)$$

The obtained mechanical parameters are tabulated in Table 4.

Table 4 The calculated bulk moduli, shear modulus G, Young's modulus E, Possion's ratio ν and anisotropy value A of Mg, Al₂ (Ca_{0.75}, Sr_{0.25}) and Al₄Sr

Material	symmetry	Moduli (GPa)				ν	A
		B	G	B/G	E		
Mg	hexagonal	35.880	19.424	1.847	49.364	0.271	0.892
		36.718 ^c					
Al ₂ (Ca _{0.75} , Sr _{0.25})	cubic	55.816	41.977	1.33	100.690	0.200	1.005
Al ₄ Sr	tetragonal	54.930	10.297	5.335	29.074	0.412	0.473

^c from Ref.[26]

The calculated elastic constants satisfy the generalized elastic stability criteria for Mg, Al₂ (Ca_{0.75}, Sr_{0.25}) and Al₄Sr. For comparison, the calculated elastic constants and mechanical parameters of Mg are listed in Table 3 and Table 4 together with the experimental results of 0 K. From Table 3 and Table 4, we can see that the obtained elastic constants and mechanical parameters of Mg were accordant with the experimental results [26].

Pugh [29] introduced the ratio of the bulk modulus to shear modulus (B/G) of polycrystalline phases as prediction of the brittle and ductile behavior of materials. A high (low) B/G value is associated with ductility (brittleness). The critical value which separates ductility from brittleness is about 1.75. From B/G calculated in Table 4 we can see that the B/G ratio of Al₂ (Ca_{0.75}, Sr_{0.25}) is the smallest, only being 1.33, indicating that Al₂ (Ca_{0.75}, Sr_{0.25}) is a brittle phase. On the contrary, the biggest B/G ratio for Al₄Sr indicates that Al₄Sr is of very good ductility in Mg–Al–Ca–Sr alloy.

Besides B/G, it was found that smaller the values of $C_{11} - C_{12}$ and Young's modulus E, better the plasticity of materials [31]. From Young's modulus E calculated in Table 4 we can see that the Young's modulus E of Al₄Sr is the smallest, only being 29.074, indicating that Al₄Sr is a plastic phase. On the contrary, the biggest E for Al₂ (Ca_{0.75}, Sr_{0.25}) indicates that Al₂ (Ca_{0.75}, Sr_{0.25}) is of poor plasticity in Mg–Al–Ca–Sr alloy.

Usually, the Possion's ratio ν is used to quantify the stability of the crystal against shear, which usually ranges from -1 to 0.5. The bigger the Possion's ratio is, the better the plasticity is. Al₄Sr has bigger Poisson's ratios, showing that Al₄Sr is of good plasticity in the investigated binary alloys. While for Al₂ (Ca_{0.75}, Sr_{0.25}), the Poisson's ratio is the smallest, corresponding to the poorest plasticity. The results from Possion's ratio ν is of very agreements with that from $C_{11} - C_{12}$ and Young's modulus E. Al₄Sr is both of the best ductility and plasticity, and Al₂ (Ca_{0.75}, Sr_{0.25}) is both of poorest ductility and plasticity in Mg–Al–Ca–Sr alloy.

All the results of the analysis on ductility and plasticity indicated that adding Ca and Sr to Mg–Al alloy could improve the ductility and plasticity by forming Al₄Sr phase, while decrease the ductility and plasticity by forming Al₂ (Ca, Sr) phase, which provides an important basis for alloys design.

Conclusions

The calculated lattice parameters and enthalpies of formation of Al₂Ca, Al₂Sr, Al₄Ca, Al₄Sr, Mg₂Ca, and Mg₂Sr phase in Mg–Al–Ca–Sr alloy system were compared with both calculation results and experimental data published in references available, and the structural stability of these intermetallic compounds phases were estimated from the energetic point of view. The results showed that Al₂Ca phase had a higher structural stability. After further calculation of lattice parameters and enthalpies of formation of Al₂(Ca,Sr) phase with Sr and Ca variation respectively, the structural stability of Al₂(Ca,Sr) phase was predicted from the thermodynamic point of view. The results showed that Al₂(Ca,Sr) phase had a good alloying ability and the Al₂(Ca,Sr) with

various Ca/Sr atom ratio was either stable, which demonstrated the mutual solubility of Ca and Sr in $\text{Al}_2(\text{Ca},\text{Sr})$ phase.

We further calculated the elastic constants and mechanical parameters for Mg, $\text{Al}_2(\text{Ca}_{0.75}, \text{Sr}_{0.25})$ and Al_4Sr in Mg–5%Al–Ca–Sr alloy, the elastic constants satisfy all the generalized elastic stability criteria for Mg, $\text{Al}_2(\text{Ca}_{0.75}, \text{Sr}_{0.25})$ and Al_4Sr . Result showed that the obtained elastic constants and mechanical parameters of Mg were accordant with the experimental results and Al_4Sr is both of the best ductility and plasticity, while $\text{Al}_2(\text{Ca}, \text{Sr})$ is both of poorest ductility and plasticity in Mg–Al–Ca–Sr alloy. All the results of the analysis on ductility and plasticity indicated that adding Ca and Sr to Mg–Al alloy could improve the ductility and plasticity by forming Al_4Sr phase, while decrease the ductility and plasticity by forming $\text{Al}_2(\text{Ca}, \text{Sr})$ phase, which provides an important basis for alloys design.

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References

- [1] Z. Yang, J.P. Li, J.X. Zhang, G.W. Lorimer, J. Robson. Review on research and development of magnesium alloys[J]. *Acta Metallurgica Sinica (English letters)*, 2008, 21(5):313-328.
- [2] E.Baril, P.Labelle, M.O.Pekguleryuz. Elevated temperature Mg–Al–Sr: Creep resistance, mechanical properties, and microstructure [J]. *Journal of the Minerals Metals & Materials Society*, 2003,55(11):A34–A39.
- [3] Huang Xiaofeng, Fu Penghuai, Lu Chen, Ding Wenjiang. Influence of Nd on the mechanical properties and high temperature creep properties of AM50 magnesium alloy [J]. *Chin J Mater Res*, 2004, 18(6):593-596.
- [4] E. F. Emley. Principles of magnesium technology [M]. Pergamon Press, Oxford, New York, ed. [1st]. 1966.
- [5] G. Nussbaum, P. Bridot, T. J. Warner, J. Charbonnier, G. Regazzoni. New Mg–Al based alloys with improved casting and corrosion properties[C]// B. L. Mordike, F. Hehmann. *Magnesium Alloys and their Application 1992*. Garmisch- Partenkirchen, Germany, 1992: 351-358.
- [6] Z. Zhang, A. Couture, A. Luo. Investigation of the properties of Mg–Zn–Al alloys [J]. *Scripta Mater*, 1998, 39:45-53.
- [7] Kinji Hirai, Hidetoshi Somekawa, Yoronobu Takigawa, Kenji Higashi. Effects of Ca and Sr addition on mechanical properties of a cast AZ91 magnesium alloy at room and elevated temperature[J]. *Materials Science and Engineering A*, 2005, 403: 276-280.
- [8] B.R. Powell, V. Rezhets, A.A. Luo, B.L. Tiwari. Creep-resistant magnesium alloy die casting [P]. US Patent, 626476324, 2001-06.
- [9] Min Xuegang, Xue Feng, Xue Feng, Sun Yangshan. The melting point of $\text{Mg}_{17}\text{Al}_{12}$ phase improved by alloyed with Ca and analysis based on the empirical electron theory (EET) [J]. *Chinese Sci Bull*, 2002, 47(2):109-112.
- [10] C. Shaw, H. Jones. Structure and mechanical properties of two Mg–Al–Ca alloys consolidated from atomized power [J]. *Mater Sci Tech*, 1999, 15(1): 78-83.
- [11] Min Xuegang, Sun Yangshan, Xue Feng, Xue Feng, Wu Dengyun. Analysis of valence

- electron structures (VES) of intermetallic compounds containing calcium in Mg-Al-based alloys [J]. *Mater Chem Phys*, 2002, 78(1): 88-93.
- [12] Zhang Wei, Liu Weidong, Wang yanchun, Zhang Shouting. Calculation of valence electron structures and analysis on strengthening mechanism of the second phase in Mg-Al-Ca alloy [J]. *Rare Metal Materials and Engineering*, 2009, 38(1):120-125.
- [13] Zhou Dianwu, Liu Jinhui, Zhang Jian, Peng Ping. Structural stability of intermetallic compounds of Mg-Al-Ca alloy [J]. *Trans. Nonferrous Met. Soc. China*, 2007, 17: 250–256
- [14] G.Kresse, J. Furthmüller. Efficient total–energy calculations basis set [J]. *Phys Rev B*, 1996,54(16) 11169–11186.
- [15] K.Schwarz, P.Blaho, G. K. H. Madsen.Electronic structure calculations of solids using the WIEN2k package of material sciences[J]. *Computer Physics Communications*, 2002:147(1-2):71-76.
- [16] D.Vanderbilt. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism [J]. *Phys Rev B*, 1990, 41(11):7892-7895.
- [17]A. Janz, R. Schmid-Fetzer. Thermodynamics and constitution of Mg-Al-Ca-Sr-Mn alloys: Part I.Experimental investigation and thermodynamic modeling of subsustems Mg-Ca-Sr and Al-Ca-Sr[J]. *Journal of Phase Equilibria and Diffusion*, 2009, 30(2): 146-156.
- [18]A. Janz, J. Grobner, R. Schmid-Fetzer. Thermodynamics and Constitution of Mg-Al-Ca-Sr-Mn Allo ys: Part II. Procedure for multicomponent key sample selection and application to the Mg-Al-Ca-Sr and Mg-Al-Ca-Sr-Mn systems [J]. *Journal of Phase Equilibria and Diffusion*, 2009, 30(2): 157-175.
- [19] W. Kohn, L.J. Sham. Perspective on “Self-consistent equations including exchange and correlation effects”[J]. *Phys Rev*, 1965, 140:1133-1138.
- [20] J.P. Perdew, K. Burke, M. Ernzerhof. Generalized gradient approximation made simple[J].*Phys Rev Lett*, 1996, 77(18):3865-3868.
- [21] G. Kresse, J.Furthmuller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set [J]. *Phys Rev B*, 1996, 54:11169-11186.
- [22] G. Kresse, J.Furthmuller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set [J]. *Comput Mater Sci*, 1996, 6:15-50.
- [23] G.Kresse, D.Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method.*Phys Rev B*, 1999, 59:1758.
- [24] E.M.Padezhnova, E.V.Melnik, R.A.Miliyevskiy, T.V.Dobatkina,V.V.Kinzhibalo. Investigation of the Mg-Zn-Y system [J].*Russ Metall*, 1982, 4(4):185–188. (In Russian)
- [25] S. Ganeshan, S.L. Shang, Y. Wang, Z.-K. Liu. Effect of alloying elements on the elastic properties of Mg from first-principles calculations[J]. *Acta Materialia*, 2009,57:3876–3884.
- [26] D. H. Chung. First pressure derivatives of polycrystalline elastic moduli: Their relation to single-crystal acoustic data and thermodynamic relations[J]. *J Appl Phys*, 1967, 38(13):5104-5113.
- [27] M. Born, K. Huang. Dynamical theory of crystal lattices[M]. Clarendon Press, Oxford, 1956.
- [28] Wu Zhijian, Zhao Erjun, Xiang Hongping, Hao Xianfeng, Liu Xiaojuan, Meng Jian. Crystal structures and elastic properties of superhard IrN₂ and IrN₃ from first principles[J]. *Physical Review B*, 2007, 76(5):054115
- [29] S.F. Pugh.Relations between the elastic moduli and the plastic properties of polycrystalline pure metals [J].*Philos Mag*, 1954, 45 (367):823-843.

- [30] H. Lic, J. L. Hoe, P. Wu. Empirical correlation between melting temperature and cohesive energy of binary Laves phases [J]. J Phys Chem Solids, 2003, 64(2): 201-212.
- [31] A. Sumer, J.F. Smith. Elastic Constants of Single - Crystal CaMg_2 [J]. J Appl Phys, 1962, 33: 2283.