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Influence of Ca addition on valence electron structure of $Mg_{17}Al_{12}$ ①

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Abstract: The alloy AZ91 containing calcium was prepared under protection of a mixed gas atmosphere of SF_6(1%, volume fraction) and CO_2. The added calcium mainly dissolves into the $Mg_{17}Al_{12}$ phase in the alloy and increases its melting point and the thermal stability. The empirical electron theory (EET) of solid and molecules was used to calculate the valence electron structures (VES) of $Mg_{17}Al_{12}$ phase with different amounts of calcium additions. The theoretical calculations indicate that calcium dissolved in $Mg_{17}Al_{12}$ phase increases the strengths of atomic bonds that control the thermal stability of $Mg_{17}Al_{12}$ phase, and also makes the distribution of valence electrons on the dominant bond network as well as in the whole unit cell of $Mg_{17}Al_{12}$ more uniform, which are consistent with the experimental results.

Key words: magnesium alloy; $Mg_{17}Al_{12}$; calcium; valence electron structure
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1 INTRODUCTION

Magnesium alloys have emerged as potentially good candidates for numerous applications, especially in automotive, aerospace and electronic industry. Their good properties, such as low density, high specific strength and good damping capacity, make them the promising replacements for other structural materials, for instance, steel, cast iron, and even aluminum[1, 2]. The widely used magnesium alloys belong to Mg-Al-Zn (AZ) series, such as AZ91 (Mg-9Al-1Zn), which have excellent castability, good room temperature mechanical properties and low cost. However, the use of these magnesium alloys has been limited because of their poor heat resistance, especially poor creep property, and its low operating temperature(only under 120 ℃)[3-8]. For the Mg-Al based alloys, $Mg_{17}Al_{12}$ is an essential phase which plays an important role in strengthening the alloys at ambient temperature. Whereas the softening of the phase at the elevated temperature is detrimental to the creep property of the alloys so that their operating temperature cannot be over 120 ℃[6]. In recent years, investigations have shown that calcium additions can improve the high-temperature properties of magnesium alloys[9, 10]. The effects of calcium addition are on two aspects: 1) Small amount of calcium addition effectively suppresses the discontinuous precipitation of $Mg_{17}Al_{12}$ in alloys[11]; 2) Calcium addition to the base alloy has the effect on enhancing of the thermal stability of the $Mg_{17}Al_{12}$ precipitates at elevated temperatures[12]. The results in the Ref.[12] show that valence electron structure of $Mg_{17}Al_{12}$ phase in the AZ91 alloy is changed with 0.3%(mass fraction) calcium addition, which increases its melting point and the thermal stability. Based on the previous work[12], the present investigation shows how the valence electron structure of $Mg_{17}Al_{12}$ phase changes with the increase of calcium addition and reveals the strengthening mechanisms of Mg-Al based alloys at the elevated temperatures caused by calcium additions.

2 EXPERIMENTAL

The alloys were prepared in mild steel crucible under the protection of mixed gas of 1%(volume fraction) SF_6 and CO_2(bal.) using commercial stock. Table 1 lists the designed and analyzed compositions of five alloys prepared. The base composition of the alloys studied was Mg-9Al-0.8Zn-0.2Mn (alloy C0) conformed to that of AZ91. The compositions of alloys C1 to C4 were based on that of AZ91 but with different amount of calcium additions. The chemical compositions of the prepared alloys were analyzed by inductively coupled plasma (ICP). The Microstructures of the alloys were characterized on selected specimens using scanning electron microscopy (SEM). Microanalysis and determination of crystal structure of different phases in the alloys were carried out by X-ray energy dispersive spectroscopy (XEDS) and X-ray

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diffractometry(XRD), respectively. The differential thermal analysis (DTA) was conducted on the specimens with different calcium additions by PEAKIN-ELMER 7 series DSC thermal analyzing system at the heating rate of 20 ℃/min.

3 RESULTS

It has been reported that the as-cast microstructure of the AZ91 alloy is composed of two phases: α-Mg and $Mg_{17}Al_{12}$[12], and small amount of calcium addition (< 0.5%, mass fraction) does not result in the formation of any new phase. In this investigation the differential thermal analysis (DTA) was conducted on the alloys to measure the melting point of $Mg_{17}Al_{12}$ phase. The DTA curves of as-cast alloys (C0, C2 and C4) are shown in Fig. 1. The point deviating from the base line corresponds to the starting point of melting, which is usually called as solidus temperature. Table 2 lists the mass fraction, molar fraction(x) of calcium in $Mg_{17}Al_{12}$ phase and the melting point of $Mg_{17}Al_{12}$ phase in the alloys studied. Both Table 2 and Fig. 1 show that solidus temperature of the alloys increased significantly with the increase of calcium additions. The highest solidus temperature obtained from alloy C4 containing 0.4% calcium reached 448.5 ℃, which is higher than that of $Mg_{17}Al_{12}$ in AZ91 alloy (424.2 ℃). This indicates that the addition of calcium increases the melting point of $Mg_{17}Al_{12}$ so that the stability of $Mg_{17}Al_{12}$ is consequently increased.

4 EMPIRICAL ELECTRON THEORY(EET)

The $Mg_{17}Al_{12}$ phase has the A12 structure (α-Mn style) with a lattice parameter of a= 1.056 nm. In the unit cell of $Mg_{17}Al_{12}$, the Mg atoms occupy three kinds of sites: Mg^{I}, Mg^{II} and Mg^{III} and its structure formula is $Mg^{I}Mg_4^{II}Mg_{12}^{III}Al_{12}$[13]. The results of the X-ray diffraction analysis show that the structure of the substitutional solid solution of $Mg_{17}Al_{12}$ containing calcium is the same as that of the solvent[12], and most of the dissolved calcium atoms are supposed to substitute for the Mg^{III} when calcium is added. The structure formula of $Mg_{17}Al_{12}$ phase with calcium additions can be written as $Mg^{I}Mg_4^{II}Mg_{12-x}^{III}Ca_xAl_{12}$ (x ranges between 0.18 and 0.75). The characteristic parameters of the hypothetic atoms which are the mass average of Mg^{III} and Ca can be shown as follows[12]:

Table 1 Chemical composition of alloys (mass fraction, %)

Alloy code	Designed composition					Analyzed composition				
	Al	Zn	Mn	Ca	Mg	Al	Zn	Mn	Ca	Mg
C0	9.0	0.8	0.2	–	Bal.	8.90	0.82	0.18	–	Bal.
C1	9.0	0.8	0.2	0.1	Bal.	–	–	–	–	–
C2	9.0	0.8	0.2	0.2	Bal.	8.80	0.80	0.20	0.22	Bal.
C3	9.0	0.8	0.2	0.3	Bal.	8.87	0.76	0.19	0.33	Bal.
C4	9.0	0.8	0.2	0.4	Bal.	8.75	0.78	0.17	0.42	Bal.

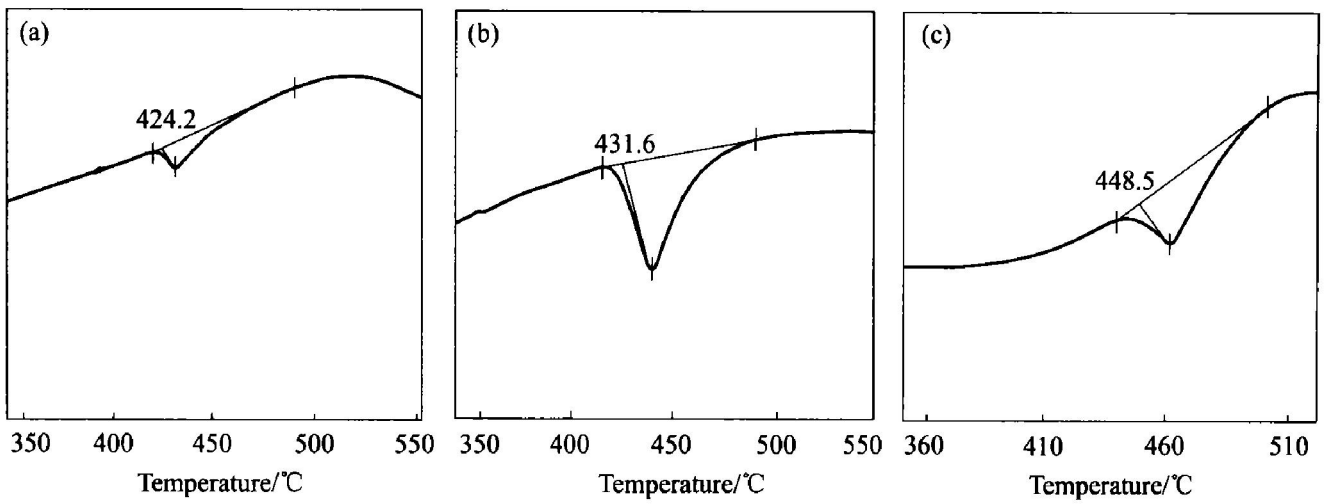

Fig. 1 DTA curves of as-cast alloys
(a) —C0 alloy; (b) —C2 alloy; (c) —C4 alloy

Table 2 Mass fraction and molar fraction of calcium in $Mg_{17}Al_{12}$ phase and melting point of alloys

Alloy code	Mass fraction of calcium/%	Melting point/℃	Molar fraction of calcium (x)
C0	0	424.4	0
C1	1.0	428.1	0.18
C2	1.8	431.6	0.37
C3	2.7	440.8	0.50
C4	3.7	448.5	0.75

$$n_c^S = x n_c^{Ca} + (1-x) n_c^{Mg^{III}} \quad (1)$$

$$n_l^S = x n_l^{Ca} + (1-x) n_l^{Mg^{III}} \quad (2)$$

$$R^S(1) = x R^{Ca}(1) + (1-x) R^{Mg^{III}}(1) \quad (3)$$

where n_c is the number of the valence electrons, n_l is the number of the crystal lattice electrons, $R^S(1)$ is half length of single bond, x is the atomic fraction of calcium in $Mg_{17}Al_{12}$ and S is the average atom of calcium and Mg^{III}.

In this study, the valence electron structures (VES) of $Mg_{17}Al_{12}$ containing different calcium content were calculated using the methods of empirical electron theory(EET)[13] and the average atom model (AAM)[12,14]. The effects of calcium addition to AZ91 on the stability of $Mg_{17}Al_{12}$ phase were also analyzed. Tables 3 and 4 list the parameters and the results of calculation, respectively. There β is a parameter, and in EET its value depends on the value of the strongest n_A in the related crystal or molecule[12].

From the results listed in Table 4, it is clear to see that the values of all five ΔD(bond length difference) are all very small, only − 0.001 3 nm, − 0.001 2 nm, − 0.000 84 nm, − 0.000 61 nm and − 0.000 14 nm, respectively, indicating that the theoretical bond length accords with the experimental bond length very well and satisfies the criterion of the empirical electron theory of solids and molecules[14]. And the calcium atoms occur at the 5th level in $Mg_{17}Al_{12}$ phase and the hybrid status of all the other atoms in $Mg_{17}Al_{12}$ containing calcium are the same as those in $Mg_{17}Al_{12}$ without calcium addition, implying that the dissolving of calcium atoms do not affect the status of primary atoms in $Mg_{17}Al_{12}$ phase.

Table 3 Parameters of analysis on valence electron structure of $Mg_{17-x}Ca_xAl_{12}$ unit cell

β	n_{c4}^{Al}	$n_{c3}^{Mg^I}$	$n_{c3}^{Mg^{II}}$	$n_{c2}^{Mg^{III}}$	n_{c5}^{Ca}
0.6	2.530	1.302 2	1.302 2	0.236 3	1.511 3
$R_{Al}(4)$	$R_{Mg^I}(3)$	$R_{Mg^{II}}(3)$	$R_{Mg^{III}}(2)$	$R_{Ca}(5)$	
0.119 0	0.126 04	0.126 04	0.127 3	0.164 4	

5 DISCUSSION

Based on the results of the VES of $Mg_{17}Al_{12}$ listed in Table 4 and the network of dominant bonds of $Mg_{17}Al_{12}$ phase (Fig. 2)[13], the integrated crystal lattice of $Mg_{17}Al_{12}$ is mainly connected by the four kinds of bonds (A, B, C and D) which are called the dominant bonds, and the structural stability of the compound is controlled by the weak bonds (C and D). Other nonessential and poor bonds only play assistant roles in the stability of the whole structure[12]. The energy of A bond and B bond in the bond network of $Mg_{17}Al_{12}$ are much

Table 4 Valence electron structure and bond energy of $Mg_{17-x}Ca_xAl_{12}$ unit cell

Alloy	Σn_c	Σn_l	I_α	D	D'_A/nm	D'_B/nm	D'_C/nm	D'_D/nm	n_A
$Mg_{17}Al_{12}$	39.701	30.299			0.265 70	0.282 12	0.290 50	0.297 77	0.345 5
$(Mg_{11.82}Ca_{0.18})Al_{12}$	39.931	30.069	12(A)	0.267 04(A)	0.265 85	0.282 35	0.290 77	0.298 07	0.343 4
$(Mg_{11.63}Ca_{0.37})Al_{12}$	40.173	29.827	24(B)	0.283 54(B)	0.266 19	0.282 69	0.291 11	0.298 41	0.339 0
$(Mg_{16.50}Ca_{0.50})Al_{12}$	40.339	29.661	24(C)	0.291 95(C)	0.266 43	0.282 93	0.291 34	0.298 65	0.335 9
$(Mg_{11.25}Ca_{0.75})Al_{12}$	40.658	29.342	48(D)	0.299 25(D)	0.266 89	0.283 39	0.291 81	0.299 11	0.330 0

Alloy	n_B	n_C	n_D	E_A/(kJ·mol^{-1})	E_B/(kJ·mol^{-1})	E_C/(kJ·mol^{-1})	E_D/(kJ·mol^{-1})	ΔD/nm
$Mg_{17}Al_{12}$	0.183 9	0.183 4	0.138 7	45.638 4	22.878 2	13.336 7	9.839 9	− 0.001 3
$(Mg_{11.82}Ca_{0.18})Al_{12}$	0.182 3	0.185 4	0.140 1	45.335 4	22.660 7	13.695 9	10.096 0	− 0.001 2
$(Mg_{11.63}Ca_{0.37})Al_{12}$	0.179 9	0.187 2	0.141 4	44.697 4	22.335 5	14.049 0	10.352 2	− 0.000 84
$(Mg_{16.5}Ca_{0.5})Al_{12}$	0.178 3	0.188 4	0.142 3	44.248 7	22.118 0	14.288 1	10.527 7	− 0.000 61
$(Mg_{11.25}Ca_{0.75})Al_{12}$	0.175 2	0.190 6	0.144 0	32.396 6	21.698 2	14.738 2	10.863 1	− 0.000 14

Bond number (A, B, C, D) correspond respectively to the bonds whose name are Al—Al, Al—Al, Al—S, Al—S; I_α is the sum of the same bond in unit cell; D is the theory bond length; D' is the experiment bond length.

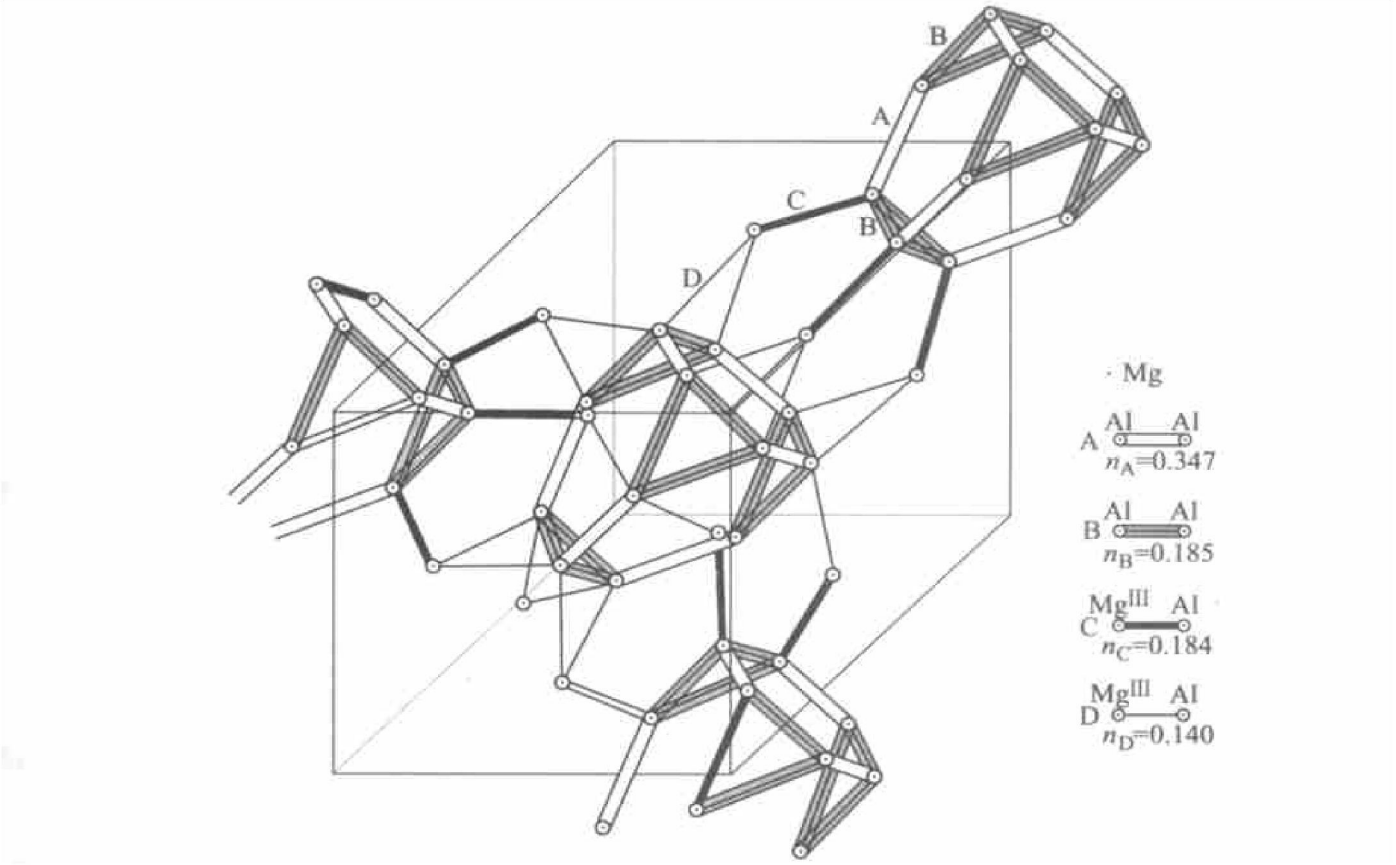

Fig. 2 Network of dominant bonds of $Mg_{17}Al_{12}$ phase[12, 13]

higher than C and D bonds. It means that the low melting point as well as low thermal stability of $Mg_{17}Al_{12}$ can be accounted for the non-uniform distribution of the valence electrons on the bond network[12]. When the dissolved calcium atoms substitute for some Mg^{III} atoms in $Mg_{17}Al_{12}$, the number of the valence electrons on C bond and D bond controlling the stability of $Mg_{17}Al_{12}$ increase continually with the increase of calcium content and the valence electrons of the strongest A bond and B bond decrease ceaselessly. The valence electrons on C bond and D bond increase by 3.9% and 4.1%, while the valence electrons on A bond and B bond decease by 4.5% and 4.7%, respectively, if the molar fraction of calcium reached 0.75. Hence, the distribution of the valence electrons on the four kinds of main bonds becomes more uniform, leading to the increase of the melting point and the thermal stability of $Mg_{17}Al_{12}$. In Table 4 it should also be noticed that the sum of the valence electrons ($\sum n_c$) in the unit cell of $Mg_{17}Al_{12}$ increased from 39.701 (without Ca addition) to 40.658(with Ca addition and its molar fraction is 0.75). Apparently, the bond between the atoms will be stronger and the melting point and the thermal stability of $Mg_{17}Al_{12}$ will be higher if there are more valence electrons on the bond.

The main factors which affect the thermal stability of $Mg_{17}Al_{12}$ have been considered to be the energy of weak bonds (C and D), the uniformity of the dominant bond network as well as the uniformity of the whole unit cell bond network of $Mg_{17}Al_{12}$[12], therefore, in this investigation E_D, B_M and B_W in the valence electron structure of $Mg_{17}Al_{12}$ phase with different calcium additions were calculated(E_D is listed in Table 4; B_M is the ratio of the sum of electrons on C bonds and D bonds controlling the structural stability to the sum of the valence electrons on four kinds of dominant bonds, and it reflects the uniformity of the dominant bond network; B_W is the ratio of the sum of the valence electrons on the four kinds of dominant bonds to the sum of the electrons in the whole unit cell, and it reflects the uniformity of the whole unit cell bond network). B_M and B_W can be calculated by using the formulas as follows:

$$B_M = \frac{I_C n_c + I_D n_D}{n_M} \tag{4}$$

$$B_W = \frac{n_M}{\sum n_c} = \frac{\sum I_\alpha n_\alpha}{\sum n_c} \tag{5}$$

Where $n_M = \sum I_\alpha n_\alpha$, and it is the sum of the valence electrons on four kinds of dominant bonds. In Table 5 the calculated results of three parameters (E_D, B_M and B_W) are listed. As shown in Table 5, with the increase of calcium content, the energy of D bond (E_D, one of the dominant parameters controlling the thermal stability of $Mg_{17}Al_{12}$

Table 5 Calcium contents and parameters of VES in $Mg_{17}Al_{12}$ phase of alloys

Alloy	E_D/(kJ·mol^{-1})	B_M	B_W
$Mg_{17}Al_{12}$	9.84	0.564	0.494
$Mg_{16.82}Ca_{0.18}Al_{12}$	10.10	0.568	0.493
$Mg_{16.63}Ca_{0.37}Al_{12}$	10.35	0.574	0.490
$Mg_{16.5}Ca_{0.5}Al_{12}$	10.53	0.577	0.487
$Mg_{16.25}Ca_{0.75}Al_{12}$	10.86	0.585	0.483

phase) increases from E_D= 9.84 kJ/mol in $Mg_{17}Al_{12}$ phase without calcium addition to E_D= 10.86 kJ/mol in $Mg_{16.25}Ca_{0.75}Al_{12}$ with calcium additions. Meanwhile, with the increase of calcium content, B_M and B_W which reflect the uniformity of the dominant bond network and the whole unit cell bond network changes. The B_M increases continually with the increase of calcium content. That is to say that calcium addition makes the valence electrons on the dominant bonds intend to distribute on the C bonds and D bonds so that the strength of these two bonds is enhanced and the strength of A bonds and B bonds is weakened. Thus the uniformity of the dominant bonds is improved. However, the B_W decreases with the increase of calcium content, from 0.494 in $Mg_{17}Al_{12}$ phase to 0.483 in $Mg_{16.25}Ca_{0.75}Al_{12}$, indicating that calcium addition decreases the sum of the valence electrons on the dominant bonds with regard to the sum of the electrons in the whole unit cell and increases the number of electrons on the sub-ordinary bonds. Hence, the whole lattice of $Mg_{17}Al_{12}$ becomes more uniform.

The relationships between the melting point of $Mg_{17}Al_{12}$ phase and the parameters are shown in Fig. 3 in which all the data have been modified by using Least-Squares-Fitting method. It can be seen that the relationships between the melting point of $Mg_{17}Al_{12}$ phase and the energy of D bond, the uniformity of the dominant bond network and the uniformity of the whole unit cell bond network are all linear, and the related coefficients(R) are all over 0.950. This indicates that these three parameters of valence electron structure are main factors affecting the melting point of $Mg_{17}Al_{12}$ phase. Among these parameters, the related coefficient between the uniformity of the dominant bond network and the melting point of $Mg_{17}Al_{12}$ phase is the highest. Its value is 0.980 implying the uniformity of the dominant bond network is most important for controlling the thermal stability of $Mg_{17}Al_{12}$ phase in AZ91 alloy.

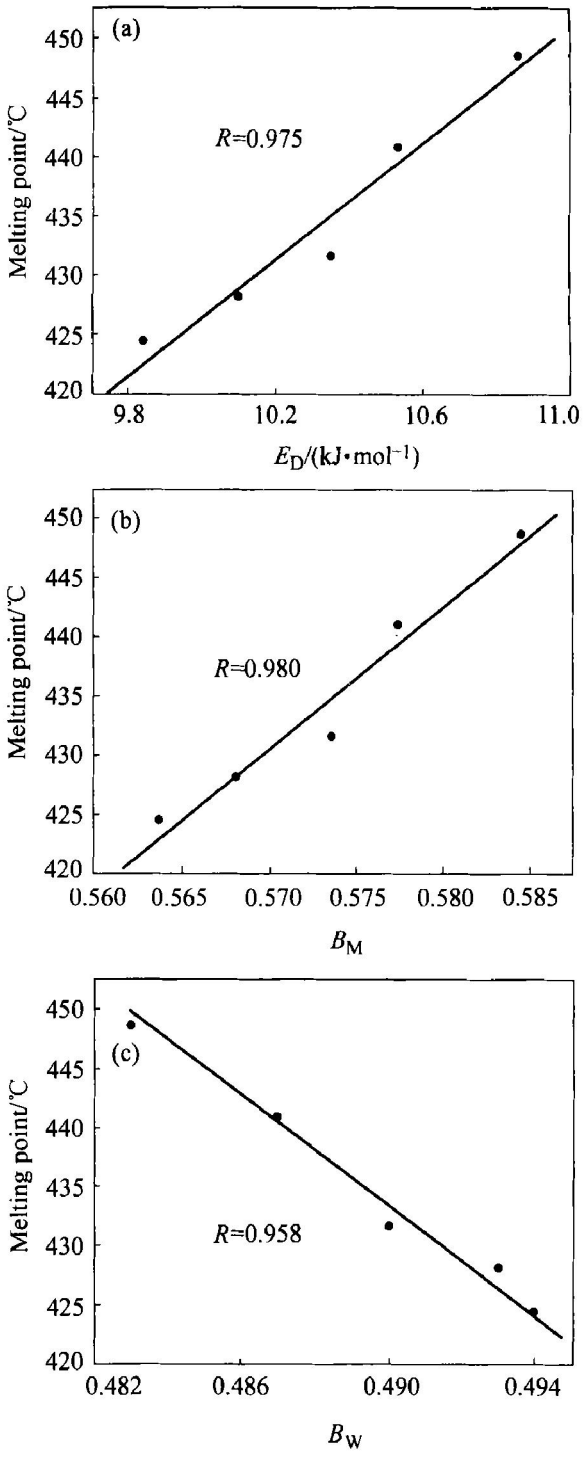

Fig. 3 Relationship between melting point of $Mg_{17}Al_{12}$ phase and parameters (a) E_D, (b) B_M and (c) B_W of valence electron structure

6 CONCLUSIONS

1) When small amount of calcium is added to the AZ91 alloy, most of the calcium atoms dissolve in $Mg_{17}Al_{12}$ phase, which leads to the increase of the melting point and the thermal stability of $Mg_{17}Al_{12}$.

2) When the molar fraction of calcium in $Mg_{17}Al_{12}$ phase alters from 0.18 to 0.75, calcium atoms all occur at the 5th level. They do not change the hybrid status of all the other atoms in $Mg_{17}Al_{12}$ and affect the status of primary atoms in $Mg_{17}Al_{12}$ phase. However, the valence electrons and bond energy of every bond are changed. The energy of two lower

bonds increases while the energy of two higher bonds decreases. The uniformity of the dominant bond network and the uniformity of the whole unit cell bond network are improved and the sum of the electrons in the whole unit cell increases.

3) The values of the three parameters(E_D, B_M and B_W) are very important factors to the thermal stability of $Mg_{17}Al_{12}$ phase. The variety of these three parameters caused by Ca addition is all beneficial to increase the thermal stability of the crystal.

4) The highest influential parameter on the thermal stability of $Mg_{17}Al_{12}$ phase is the uniformity of the dominant bond network(B_M) indicating the raise of the melting point and the thermal stability of $Mg_{17}Al_{12}$ phase caused by Ca addition is mainly accounted for by the improvement of the uniformity of the dominant bond network.

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