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ARTICLE

Interfacial Reaction Between Mg-40Al and Mg-20Ce Using Liquid-Solid Diffusion Couples

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Abstract: Interfacial reactions and growth kinetics between molten Mg-40Al and solid Mg-20Ce were investigated. Reaction temperatures were 475, 500 and 525 °C, with reaction time ranging from 5 to 30 min. The results show that $Al_{11}Ce_3$, Al_3Ce and Al_2Ce are formed via the reaction of Al and Ce in the diffusion reaction layers. The volume fraction of the intermetallic compounds in the diffusion reaction layers increases with temperature increasing. The growth kinetics of the diffusion reaction layers well conform to the parabolic law. The activation energy for the growth of the diffusion reaction layers is (42±3.7) kJ/mol. Liquid-solid diffusion experiment helps to better understand the formation of compounds in the smelting process. Kinetics data are provided for the formation of the compound during the smelting process.

Key words: magnesium; diffusion; interface; intermetallic compounds; kinetics

Diffusion plays a critical role in solidification, precipitation, homogenization, dissolution, protective coatings, and creep. Systematic studies on diffusion can help to find reliable parameters, which can guide the final product design to obtain the desired microstructure and mechanical properties[1]. Magnesium alloys are one of the most attractive options for a promising application in the automotive and aircraft industries, due to their high specific strength, excellent castability, and excellent machinability[2, 3]. Mechanical properties of magnesium alloys are improved by precipitation strengthening[4], while the study of precipitation process demands accurate kinetic data. Due to surface oxidation during sample preparation in diffusion measurements[5], the diffusion of alloying elements in Mg has not been very well investigated yet. The current commercial use of magnesium alloys is mainly focused on Mg-Al based alloys. However, Mg-Al alloys have been mainly restricted to room-temperature applications due to the poor creep resistance of the alloys[6]. The addition of Cerium (Ce) to the Mg-Al alloys is well known to improve its strength by the formation of relatively thermally stable Al-Ce intermetallic compounds[7,8]. However, the high temperature formation of Al-Ce intermetallic compounds is still unknown. Therefore, to understand the formation of Al-Ce intermetallic compounds in Mg-Al-Ce alloys through the diffusion method is important.

Previously, there are a great number of studies about the phase type in Mg alloys through the diffusion method[9-12]. The Ce-Mg-Zn phase diagram at 350 °C was studied by diffusion couple techniques[13]. Precipitation of intermetallic compounds in the Mg-rich region was analyzed. A solid-liquid contact method was employed to produce the Mg_2Ce and Al_2Ce diffusion couples in the Al-Mg-Ce system[14]. The prepared samples were annealed

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at 400 °C for 4 weeks. Three compounds were identified: BCC_B2, Laves_C15 and the Al_2Ce compound. Recently, the authors used the solid-solid diffusion couples experiments to determine the form of the Al-Ce intermetallic compounds at (Mg-Al)/(Mg-Ce) interfaces[15]. However, no studies systemically investigated the diffusion kinetics of the formation for Al-Ce intermetallic compounds in Mg melt.

Compared with solid-solid diffusion, the liquid-solid diffusion couple interface is easy to combine, and diffusion annealing time is short[16], and the formation of intermetallic compounds during the smelting process can be understood. Therefore, the present work employs the diffusion couple technique and involves a detailed diffusion reaction study between Mg-40Al melt and solid Mg-20Ce matrix in the temperature range of 475~525 °C. The growth kinetics of the diffusion reaction layer was determined simultaneously.

1 Experiment

Pure Mg (99.99 wt%), pure Al (99.99 wt%) and Mg-20Ce (Mg-20 wt% Ce) master alloy were used. Al was added to Mg to form Mg-40Al (Mg-40 wt% Al) master alloy. A rectangular piece of Mg-20Ce master alloy was polished with 200-grit SiC paper. The Mg-40Al master alloy was placed in a mild steel crucible with a diameter of 8.5 mm and a length of 15 mm and melted under a SF_6 and CO_2 protective atmosphere, and maintained at the experimental temperature for melting before the Mg-20Ce master alloy was introduced into the molten material. Then the Mg-20Ce master alloy was immediately submerged into the molten Mg-40Al material. The samples were heated to 475, 500 and 525 °C. The heat treatment time of each temperature is 5, 10, 20 and 30 min under a cover gas of SF_6 and CO_2. A schematic diagram of the diffusion couple preparation procedures is shown in Fig.1. After the required reaction time, the crucibles along with the samples were quenched in cold water for obtaining the high temperature structure.

The samples were cut exactly perpendicular to the diffusion contact plane using wire electrical discharge machining and ground with grinding papers from 200, 400, 600, 800 to 1000 grit. Each diffusion couple was examined under an optical microscope to make sure that the reaction layers are perfect, and then the diffusion reaction layers of the good samples were examined using Scanning Electron Microscopy (SEM, TESCAN VEGAⅡLMU). The intermetallic compounds were identified by X-ray Diffractometer (XRD, Rigaku D/max 2500PC), Transmission Electron Microscope (TEM, Tecnai G2F20 S-TWIN) equipped with Energy Dispersive Spectroscopy (EDS, OXFORD) and Differential Scanning Calorimeter (DSC, NETZSCH-STA499C). DSC runs were carried out at cooling rate of 10 °C/min under a dynamic argon atmosphere. To determine the growth kinetics of the diffusion reaction layers, the thicknesses of the diffusion reaction layers were examined from SEM micrographs of the cross-sections. An average thickness was obtained from 10 individual measurements.

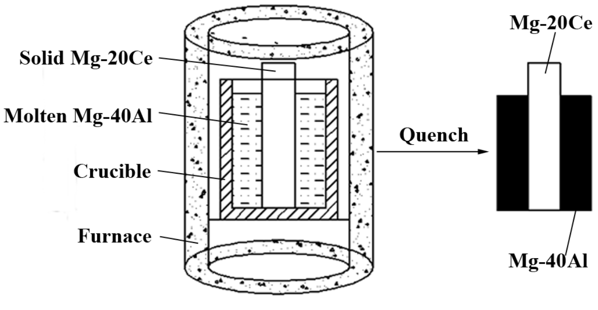


Fig.1 A schematic diagram of the diffusion couple preparation procedures

2 Results and Discussion

2.1 Microstructural of the diffusion reaction layers

Fig.2a~2c show Backscattered Electron (BSE) images of the different reaction layers formed in the diffusion couples annealed at 475, 500 and 525 °C for 10 min, respectively. It is observed that the reaction layer exists between the two matrices and the crack-like lines are observed in the diffusion couples because of the brittleness of the diffusion reaction layer. The average thickness of the diffusion reaction layer increases with respect to temperatures, which is about 375, 563 and 882 μm, respectively, and volume fraction of the intermetallic compounds in the diffusion reaction layer increases as well. No sub-layer exists in the diffusion reaction layers of the liquid-solid diffusion couples. However, the average thickness of the diffusion reaction layer for the (Mg-Al)/(Mg-Ce) solid state diffusion couple is about 200 μm at 400 °C for 72 h, and several reaction sub-layers are observed to form at the interfaces[15]. Compared with time, the influence of temperature is more significant in diffusion process.

To identify the intermetallic compounds in the diffusion reaction layers, XRD examination was carried out after the diffusion reaction layer was ground down to the corresponding depth. Fig.3 shows a schematic diagram of the XRD samples preparation procedures and XRD results of the diffusion reaction layers for the diffusion couples annealed at 475, 500 and 525 °C for 10 min. The XRD results reveal that in addition to the Al-Ce intermetallic compounds of $Al_{11}Ce_3$, Al_3Ce and Al_2Ce, there also exist $Mg_{41}Ce_5$, $Mg_{17}Ce_2$ and $Mg_{12}Ce$ compounds in the XRD samples. The XRD peak quantity of $Al_{11}Ce_3$ is significantly higher than those of the other intermetallic compounds. It can be

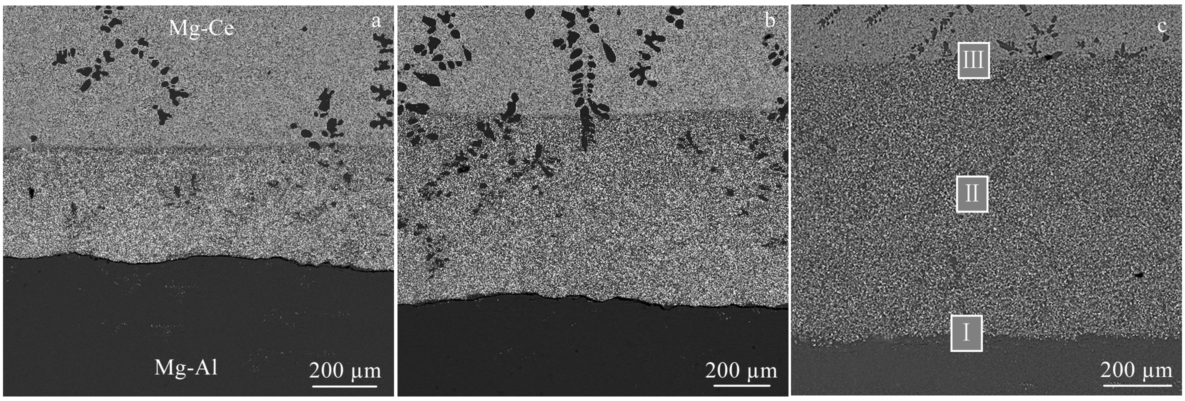


Fig.2 SEM images of the diffusion reaction layers for the diffusion couples annealed at different temperatures for 10 min: (a) 475 °C, (b) 500 °C, and (c) 525 °C

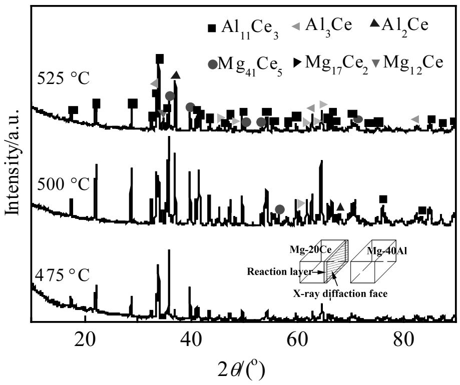


Fig.3 XRD patterns of the reaction product after annealing at different temperatures for 10 min (insets is the schematic image of the XRD samples preparation procedures)

concluded that the quantity of $Al_{11}Ce_3$ is higher than other intermetallic compounds in the diffusion reaction layer. Further investigations are required to elucidate the formation of the intermetallic compounds.

To further study the intermetallic compounds in the diffusion reaction layer, regions I-III in Fig.2c were observed using higher magnification BSE, as shown in Fig.4a~4c. In regions I~III, the intermetallic compounds are mainly tiny particles. So the TEM was used to analyze them. Fig.5 shows the Bright Field (BF) image and EDS analysis of the diffusion reaction layer for the diffusion couple annealed at 525 °C for 10 min. It can be seen that several particle-like intermetallic compounds are distributed in the diffusion reaction layer. Region 1 is a liquid phase, because the diffusion couple is quenched. Region 2 is a coarse particle-like intermetallic compound with an atomic ratio of Al/Ce=2.29. It can be concluded that region 2 is Al_2Ce. Region 3 is an irregular particle-like intermetallic compound with an atomic ratio of Al/Ce of 2.97. It can be concluded that region 3 is Al_3Ce. Region 4 is particle-like intermetallic compound with an atomic ratio of Al/Ce of 3.46. It can be concluded that region 4 is $Al_{11}Ce_3$. Nevertheless, $Mg_{41}Ce_5$, $Mg_{17}Ce_2$ and $Mg_{12}Ce$ compounds are not detected in diffusion reaction layers, which are located on the Mg-20Ce matrix (Fig.4c). Combined with microstructure and EDS results of the intermetallic compounds, it can be concluded that the intermetallic

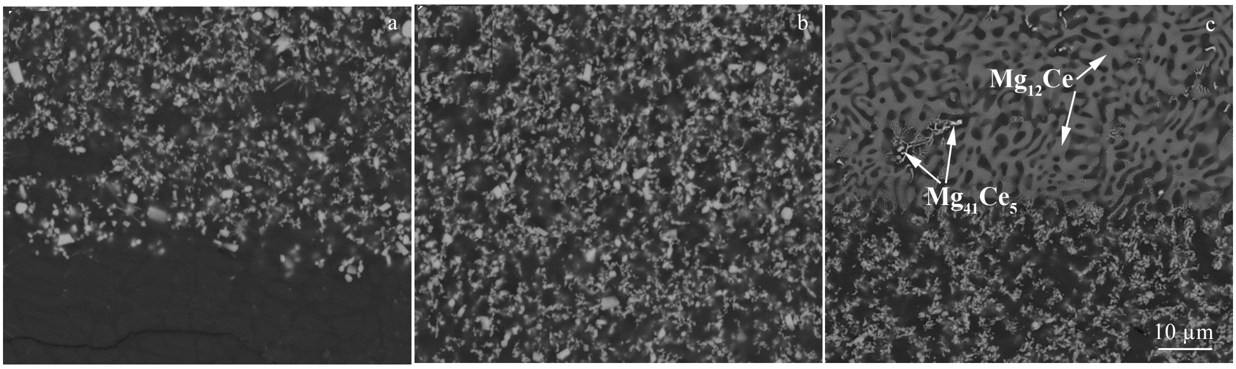
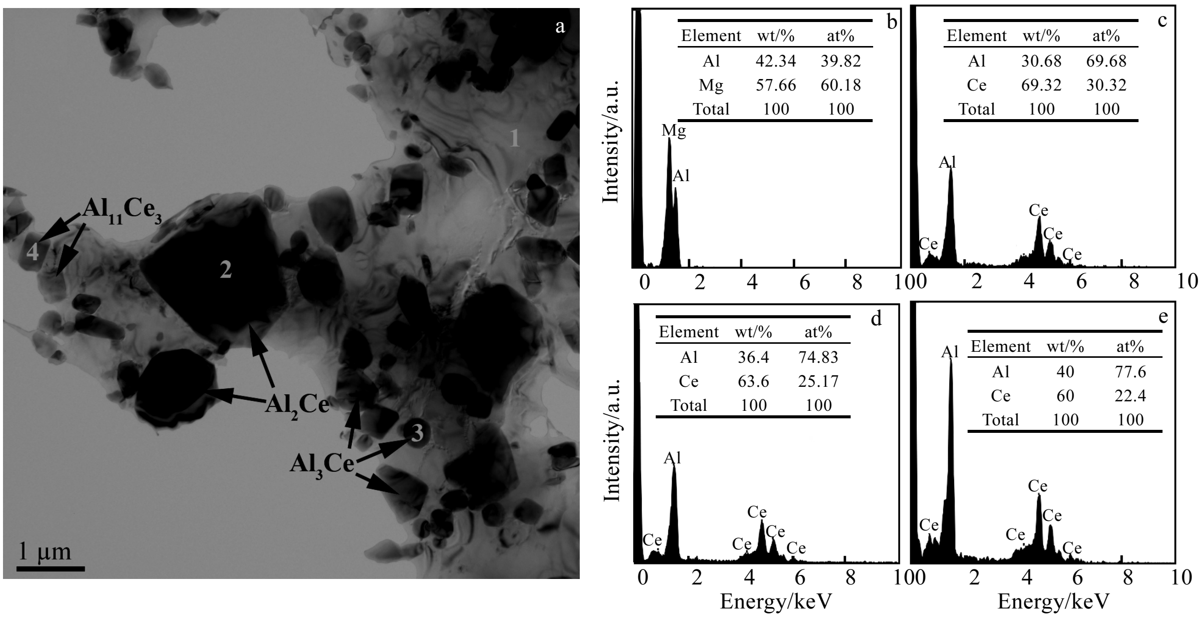


Fig.4 High magnification images of region I (a), region II (b), and region III (c) from Fig.2c



Element	wt/%	at%
Al	42.34	39.82
Mg	57.66	60.18
Total	100	100

Element	wt/%	at%
Al	30.68	69.68
Ce	69.32	30.32
Total	100	100

Element	wt/%	at%
Al	36.4	74.83
Ce	63.6	25.17
Total	100	100

Element	wt/%	at%
Al	40	77.6
Ce	60	22.4
Total	100	100

Fig.5 TEM image of the diffusion reaction layer for the diffusion couples annealed at 525 °C for 10 min (a); (b), (c), (d) and (e) are EDS results of point 1, 2, 3 and 4 in Fig.5a, respectively

compounds are mainly Al-Ce intermetallic compounds in the diffusion reaction layer. Because the mixing enthalpy of Al and Ce is more negative than that of Mg-Al or Mg-Ce[17], Al-Ce intermetallic compounds have high chemical stability, Ce are combined with Al and form Al-Ce intermetallic compounds without any formation of pseudo binary Mg-Ce phase until all the available Ce are used.

Fig.6 shows the DSC cooling curve of diffusion reaction layer for the diffusion couple annealed at 525 °C for 10 min. During continuous cooling in DSC, two endothermic peaks appear, at about 419.31 and 429.25 °C. The concentration of Mg and Al in the diffusion reaction layer are 47.80wt% ~58.42wt% and 35.73wt%~24.42wt%, respectively. From Mg-Al phase diagram[18] (Fig.9a), the melting point of alloy for the diffusion reaction layer is about 500 °C, or even lower. According to previous research on the AZ91D alloy[19], $Mg_{17}Al_{12}$ precipitates at 419.3 °C and follows the α-Mg, when the cooling rates is 10 °C/min. In addition, $Al_{11}Ce_3$ and Al_2Ce prior to the α-Mg precipitate in AM60-1.5Ce alloy[20] and Mg-6Ce-3Al alloy[21], respectively. It can be speculated that the exothermic peak at about 419.31 °C corresponds to the formation of Mg17Al12, and the peak at about 429.25 °C corresponds to the formation of α-Mg. This suggests that the Al-Ce intermetallic compounds form in Mg melt.

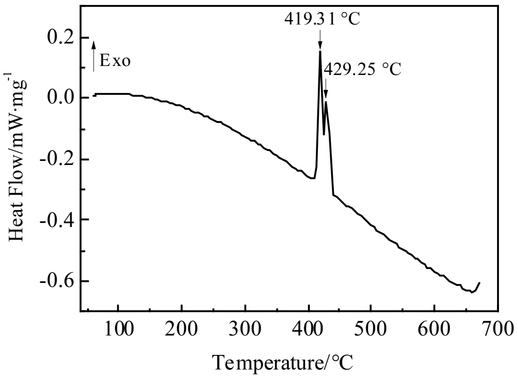


Fig.6 DSC cooling curve of the diffusion reaction layer for the diffusion couple annealed at 525 °C for 10 min

2.2 EDS analyses of the diffusion reaction layers and diffusion path

Fig.7 shows composition profiles across diffusion reaction layers examined by EDS line scanning with a spatial size of 35 μm for the diffusion couples annealed at 475, 500 and 525 °C for 10 min. The concentration of Mg in the diffusion reaction layers is significantly lower than that in the Mg-20Ce matrix which decreases gradually from the Mg-20Ce matrix to the Mg-40Al matrix. The distribution of Al is decreased gradually from the Mg-Al matrix to the diffusion reaction layers. The concentration profile of Ce is almost flat from the Mg-20Ce matrix to the diffusion reaction layers. Fig.8 shows the distribution of Mg, Al and Ce elements in the interface of the diffusion couple at 525 °C for 10 min. These results are consistent with the results of EDS line scanning. It suggests that the diffusion of Al is faster than that of Ce in Mg, which may be related to the state of Mg-40Al and Mg-20Ce matrices at experiment temperature. Mg-Al[18] and Mg-Ce[22] binary phase diagrams are shown in Fig.9. The binary phase diagrams suggest that the Mg-40Al master alloy is liquid and

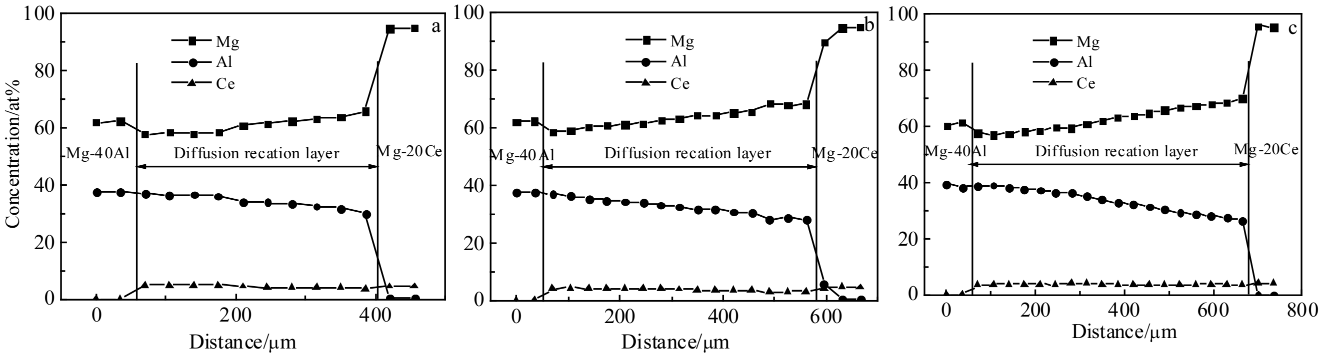


Fig.7 Composition profile images of diffusion reaction layers for the diffusion couple annealed at different temperatures for 10 min: (a) 475 °C, (b) 500 °C, and (c) 525 °C

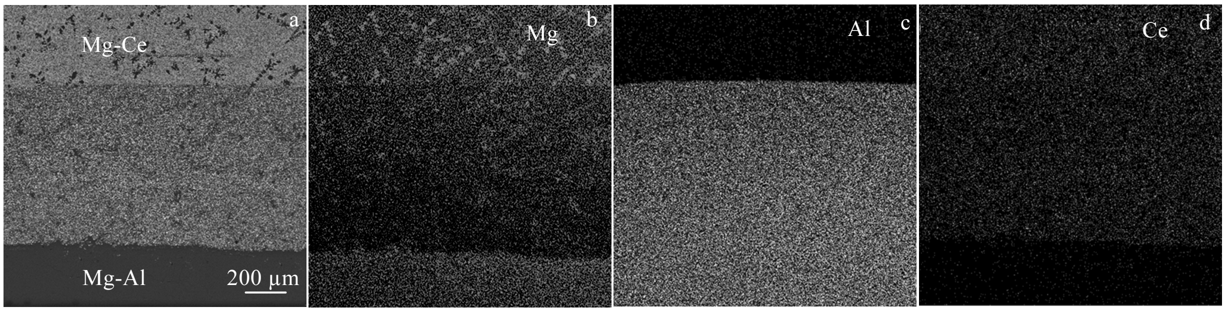


Fig.8 SEM image (a) and EDS element mapping of diffusion couple at 525 °C for 10 min: (b) Mg, (c) Al, and (d) Ce

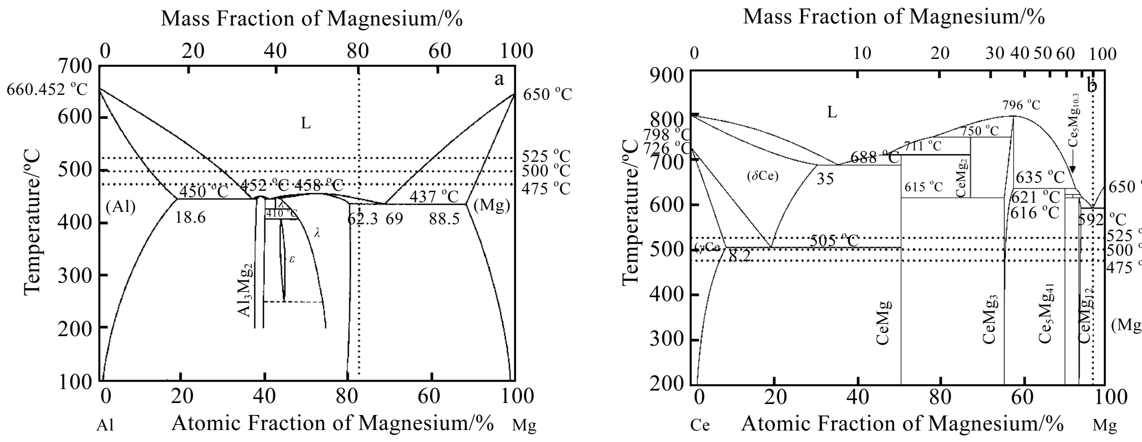


Fig.9 Binary phase diagrams of Mg-Al (a) and Mg-Ce (b)

the Mg-20Ce master alloy is solid in this experiment temperature range. Therefore, Al atoms in molten Mg-40Al are more active than Ce atoms in solid Mg-20Ce matrix.

Microstructural and compositional development from the diffusion couples can be described by the diffusion paths drawn on the isothermal ternary phase diagram. Fig.10 shows the semi-quantitative diffusion paths estimated for the diffusion couples annealed at 475, 500 and 525 °C for 10 min. The experimental results are mainly located in $Al_{11}Ce_3$ phase region.

2.3 Growth behavior of the diffusion reaction layers

It is important to clarify the growth kinetics of these diffusion reaction layers for the design and control of Al-Ce intermetallic compounds. Here, we observed in detail the growth of diffusion reaction layers at temperature 475~525 °C.

Fig.11 shows the relationships between the thickness of diffusion reaction layers and the square root of diffusion

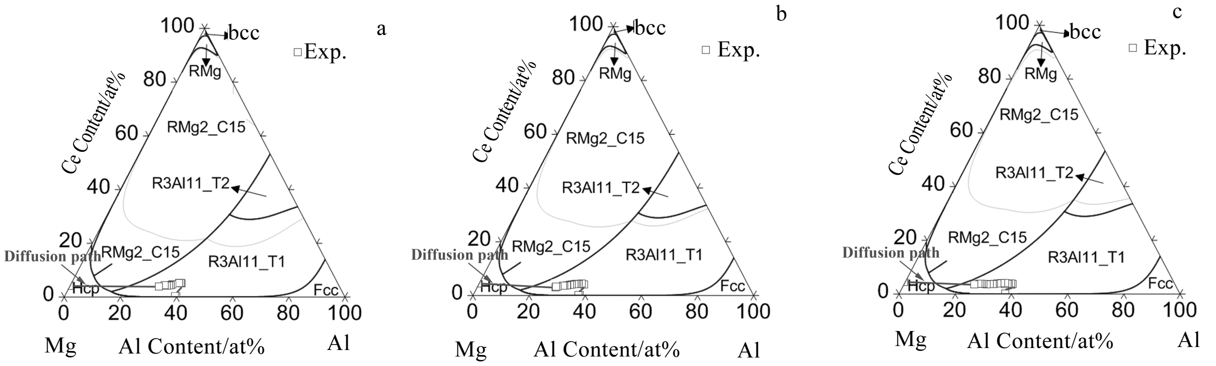


Fig.10 Calculated isothermal section of Mg-Al-Ce ternary system with diffusion paths at 475 °C (a), 500 °C (b), and 525 °C (c)

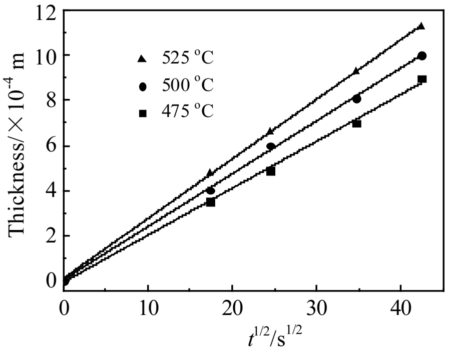


Fig.11 Relationship between the thickness of the diffusion reaction layers and the square root of treatment time for all the diffusion couples

time for the specimens which were diffusion-treated at 475, 500 and 525 °C. It can be seen the linear fit to the experimental data point scan reach the origin, and most of the linear correlation coefficient values (R^2) for these plots are higher than 0.99, which proves that the nucleation time is negligible compared with the annealing time. It is suggested that the thickness of the layers demonstrates a linear relationship with the square root of diffusion time. It is well known that the equation of such growth:

$$d = (kt)^{1/2} \tag{1}$$

where d is the thickness of the diffusion reaction layer in meter and t is the diffusion reaction time in second, and k is the growth constant in m^2/s.

The following Arrhenius-type relationship is used to determine the apparent activation energy for diffusion controlled growth:

$$k = k_0 \exp\left(\frac{-Q}{RT}\right) \tag{2}$$

where k_0 is the pre-exponential factor, Q is the activation energy, R is the gas constant, and T is the absolute temperature. The activation energy can be obtained from the plots of ln(k) versus the reciprocal of temperature T, as shown in Fig.12. With Eq.(1) and (2), the growth rates, activation energy and pre-exponential factor of the diffusion reaction layers are calculated. At 475, 500 and 525 °C, the growth constants of entire diffusion reaction layer are calculated to be $(4.63\pm0.81)\times10^{-10}$, $(5.57\pm0.76)\times10^{-10}$, $(7.08\pm0.39)\times10^{-10}$ m^2/s, respectively. The order of magnitude for growth constants matches well within an order of magnitude for liquid diffusion coefficient. The growth constants are higher than that in previous study of the solid-state diffusion reaction for (Mg-Al)/(Mg-Ce) diffusion couples[15], which may be related to the annealing temperature. The calculated apparent activation energy for the growth of the total diffusion reaction layer is (42±3.7) kJ/mol. The pre-exponential factor for the growth of the entire diffusion reaction layer is determined to be $(3.97\pm0.67)\times10^{-7}$m^2/s.

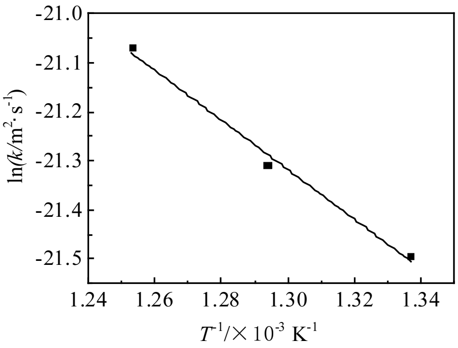


Fig.12 An Arrhenius plot of the diffusion reaction layer growth

3 Conclusions

1) Development of intermetallic compound constituents, microstructure, concentration profiles and growth kinetics between molten Mg-40Al and solid Mg-20Ce diffusion couples were investigated at 475, 500 and 525 °C, with reaction time ranging from 5 to 30 min. During the whole diffusion process, Al-Ce intermetallic compounds of $Al_{11}Ce_3$, Al_3Ce and Al_2Ce form in the diffusion reaction layer. The concentration profiles projected as

semi-quantitative diffusion paths on an Mg-Al-Ce isothermal ternary phase diagram agree in general with the experimental results.

2) The relationships between each layer thickness and reaction time follow the parabolic law. The temperature dependence of growth of the diffusion reaction layers conforms to an Arrhenius relation. At 475, 500 and 525 °C, the growth constants of the total diffusion reaction layers are $(4.63\pm0.81)\times10^{-10}$, $(5.57\pm0.76)\times10^{-10}$, $(7.08\pm0.39)\times10^{-10}$ m^2/s, respectively. The activation energy for the growth of the total diffusion reaction layer is calculated to be (42±3.7) kJ/mol.

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基于固液扩散偶研究 Mg-40Al 与 Mg-20Ce 的界面反应

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摘 要：研究了 Mg-40Al 与 Mg-20Ce 固液界面在 475、500 和 525 ℃下保温 5~30 min 的界面反应和扩散层的生长动力学。结果发现，在扩散层中由于 Al 元素和 Ce 元素反应生成 $Al_{11}Ce_3$、Al_3Ce 和 Al_2Ce 金属化合物。金属化合物的体积分数随着扩散温度的升高而增加。扩散层的生长满足抛物线生长规律，扩散层的扩散激活能为(42±3.7) kJ/mol。实验研究的固液扩散为理解合金熔炼过程中金属化合物的形成提供了理论基础。

关键词：镁；扩散；界面；金属合金物；动力学

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