First experimental measurement of calcium diffusion in magnesium using novel liquid-solid diffusion couples and forward-simulation analysis

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Abstract

A novel liquid-solid diffusion couple enables effective measurements of composition profiles at high temperatures. A forward-simulation analysis is then performed to extract both interdiffusion and impurity diffusion coefficients. The combined method enables measurement of the first ever set of impurity diffusion coefficients of Ca in Mg and reliable high-temperature diffusion data of Al in Mg. *The results show that Ca diffuses faster than the Mg self-diffusion which is faster than the Al diffusion in Mg; thus Ca may not be an ideal element for the enhancement of high-temperature creep strength of Mg alloys as has been often assumed.*

Keywords: Magnesium alloys; Calcium; Aluminum; Impurity diffusion coefficient; Interdiffusion coefficient

Mg alloys with low densities and high specific strength are promising materials for vehicle lightweighting applications [1–3] to improve fuel efficiency and reduce CO₂ emission. Utilization of Mg alloys in vehicles is still limited compared to steels and Al alloys [4,5] mostly due to a few inadequate properties such as low creep strength and poor formability [6]. Advanced Mg alloys with improved properties are being pursued worldwide to expand the application of Mg alloys in vehicle lightweighting.

The Integrated Computational Materials Engineering (ICME) approach is an efficient way for innovation in advanced materials [7]. Both thermodynamic databases and diffusion (mobility) databases are the foundations for ICME alloy design. Although the thermodynamic databases of Mg-based systems are relatively complete [8–11], only one very preliminary mobility database

for Mg alloys was published recently [12]. The reliability of this mobility database is limited since no experimental diffusion coefficients were available for several key alloying elements.

Experimental diffusion coefficients are essential input to the establishment of reliable diffusion/mobility databases, but very limited experimental diffusion data of Mg alloys are available. Most diffusion studies in Mg-based systems have been performed on the Mg-Al system [13–17] while no experimental diffusion data are available for Ca which is another important alloying element in Mg alloys.

The impurity diffusion coefficients are traditionally measured using tracer experiments which are tedious and not applicable for some elements such as Al and Ca that do not have suitable radioactive isotopes. Very dilute alloys can be used to make the so-called incremental solid-solid diffusion couples with pure elements to obtain impurity diffusion coefficients; however, such a method is not easily applicable for many Mg-based systems since it is difficult to make exact alloy compositions of extremely dilute Mg alloys with elements such as Ca, Sr, and Nd. The limitation of traditional experimental techniques for diffusion coefficient evaluation calls for innovation of methods to measure diffusion data reliably for Mg alloys.

In this study, a novel liquid-solid diffusion couple (LSDC) geometry intentionally takes advantage of the liquid phase formation at annealing temperatures above the eutectic point to study diffusion in the Mg-Al and Mg-Ca binary systems by forming a small liquid pool contained inside a relatively large block of pure Mg, as shown in Fig. 1. Pure Mg (99.95 wt.%), Al (99.95 wt.%), Fe (99.9 wt.%), and a Mg-15 wt.%Ca master alloy were used to assemble the LSDCs. All pieces were prepared to the desired dimensions by mechanical machining or electrical discharge machining (EDM) and grinded to a fine surface finishing. A 5-mm diameter hole is drilled into a solid pure Mg block (20 x 20 x 25 mm) to a depth of ~18 mm with a milled flat bottom. A screw thread is made at the top neck of the hole. Pure Al or the Mg-15 wt.%Ca master alloy (marked as M in Fig. 1(a)) along with pure Mg and pure Fe are machined into 5-mm diameter cylinders/pellets with a height of ~3 to 5 mm. These pellets are put into the hole in sequence as shown in Fig. 1(a). A carbon steel screw is applied at the top to tighten the diffusion couple assembly, which promotes the initial contact between the pellets below. The whole assembly process is performed inside a high-purity argon glovebox with an oxygen and water vapor level of < 0.3 ppm and < 0.5 ppm, respectively. The tightened screw threads prevent air from reaching inside the diffusion couple when the sample is taken out of the glovebox. The

sample is then sealed inside an evacuated quartz tube backfilled with 1/5 atmosphere pressure of high-purity argon to prevent oxidation during diffusion annealing. Effort is made to shorten the time between diffusion couple assembly and encapsulation into quartz tubes.

The pure Fe cylinder prevents carbon and other impurities in the carbon steel screw from diffusing into the middle Mg piece since Fe has no solubility in Mg and the diffusion of carbon and other elements in Fe is too slow at the diffusion annealing temperatures and time durations to reach the bottom of the pure Fe piece. The middle Mg piece is added such that the bottom metal (M) piece only interacts with Mg in every direction, making a very clean Mg-M LSDC. The Mg-M region melts when the sample is heated at a temperature above their eutectic point. Diffusion takes place between the liquid phase and Mg to form an Mg solid solution in the region adjacent to the small liquid pool formed in the center. After certain duration of diffusion annealing, the LSDC is quenched to room temperature by breaking the quartz tube into a small water tank.

Figure 1(c) is an example of a sectioned LSDC after diffusion heat treatment, showing the solidified liquid phase in the bottom center of the sample. The diffusion heat treatment conditions are 450 °C 8 h, 500 °C 6 h, 550 °C 6 h, and 600 °C 4 h respectively for the Mg-Al LSDCs; and 530 °C 50 h, 580 °C 24 h, 600 °C 20 h, 630 °C 13 h respectively for the Mg-Ca LSDCs. The LSDCs were then cut through center line and metallographically prepared for characterizations using optical microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The diffusion profiles were quantitatively measured using a CAMECA SX100 electron microprobe operated at 15 kV accelerating voltage, 30 nA beam current, and a 40° take-off angle. The EPMA step sizes varied among samples, from 1 μm to 5 μm depending on the width of the diffusion zone. A SEM image in Fig. 1(d) shows the liquid-solid boundary of an Mg-Ca LSDC after being annealed at 630 °C for 13 h.

Figure 2(a) shows the EPMA results of the Mg-Al LSDCs that were annealed at 450 °C, 500 °C, 550 °C and 600 °C respectively. The smooth profiles on the left are the Mg solid solution with a varying Al concentration across the diffusion zone. The arrow in Fig. 2(a) indicates the solubility of Al in Mg at 500 °C, which can be precisely determined from the diffusion profile. The solubility at 450 °C, 500 °C, 550 °C and 600 °C is determined to be 10.3, 7.2, 4.6, and 2.5 at.% Al, respectively; consistent with the Mg-Al binary phase diagram.

The measured composition of the solidified liquid phase (compositions beyond the single-phase Mg solid solution in Fig. 2(a)) shows a large variation due to the segregation upon

quenching and the formation of the solidified two-phase eutectic microstructures (e.g., [Fig. 1\(d\)](#)). The traditional Boltzmann-Matano analysis [18] and the Sauer-Freise method [19] cannot be applied to evaluate diffusion coefficients when one end of the diffusion profiles has widely varying compositions. A forward-simulation analysis recently developed by Zhang and Zhao [20,21] can reliably evaluate both interdiffusion and impurity diffusion coefficients and is applied to analyze the diffusion profiles of LSDCs.

Since the diffusion coefficients of the liquid phases are usually very high, on the order of 10^{-9} to 10^{-8} m²/s, it is safe to assume that the composition of the liquid phase is homogeneous at the annealing temperature. An assumption is also made that the liquid composition interfacing with the boundary of the Mg solid solution is the equilibrium liquidus composition defined by the corresponding binary phase diagram at the annealing temperature. Forward simulations were performed to test the effect of the assumed liquid composition on the extracted diffusion coefficients by varying the liquid composition from 10 at.% above or below the liquidus composition at the annealing temperature. The extracted diffusion coefficient was found to vary only by about 8%. This is because the diffusion in the Mg solid solution is predominately dictated by the slow diffusion process within the solid itself and the adjacent liquid essentially serves as a reservoir for the solute. With the described assumptions, the forward-simulation analysis can be readily applied to extract diffusion coefficients from the diffusion profiles obtained from LSDCs.

The excellent agreement between the simulated concentration profiles and the experimental data indicates that the determined diffusion coefficients of the Mg-Al hcp phase are reliable, [Fig. 2\(a\)](#). The obtained interdiffusion and impurity diffusion coefficients are summarized in [Fig. 2\(b\)](#) and [2\(c\)](#); and are compared to prior literature data.

Kammerer et al. [17] employed the Boltzman-Matano analysis and the Hall method [22] to determine both the interdiffusion coefficients and impurity diffusion coefficients of the Mg-Al binary system from solid-solid diffusion couples made up of pure Mg and Mg-Al alloys. Our results at 450 °C agree well with those reported by Kammerer et al. at the same temperature as shown in [Fig. 2\(b\)](#); and our data are consistent with this independent study in terms of the trend for both interdiffusion and impurity diffusion coefficients, demonstrating the reliability of the combined LSDC and forward-simulation approach. Our results extend the credibility of

experimental diffusion coefficients of the Mg-Al system to much higher temperatures than the prior literature results.

Brennan et al. used secondary ion mass spectrometry (SIMS) [23] to obtain the depth profiles from samples annealed at 300 °C to 400 °C [13]. They admitted that their data were higher than actual values due to grain boundary diffusion and sputter roughening which is an inherent limitation of SIMS. They subsequently employed traditional diffusion couples to perform another study at the same temperature range [14] and extrapolated the interdiffusion coefficients at the Mg-rich side to estimate the Al impurity diffusion coefficients which are comparable to those of the present study as well as the results from Kammerer et al., Fig. 2(c).

There is general agreement in the experimental impurity diffusion coefficients from three independent investigations: the present study, the diffusion couple results from Kammerer et al. [17], and the diffusion couple data from Brennan et al. [14], as shown in Fig. 2(c). These datasets are used to obtain a best-judgement/consentaneous impurity diffusion coefficient of Al in Mg as the solid red line in Fig. 2(c) and as represented by an Arrhenius equation $D_{Al\ in\ Mg} = 2.4 \times 10^{-4} e^{-146800/RT}$ (in m²/s with T in Kelvin and $R = 8.314\ J\ K^{-1}\ mol^{-1}$). Our data lend credibility to this overall impurity diffusion coefficient equation by providing reliable high temperature data to support the results from both Kammerer et al. [17] and Brennan et al. (diffusion couple data) [14]; and together the trend in Fig. 2(c) indicates that the SIMS results from Brennan et al. [13] and the diffusion couple results reported by Das et al. [15] are too high and are questionable.

Since pure Ca is extremely easy to oxidize and highly hydroscopic, a Mg-15 wt.% Ca master alloy is used to assemble four Mg-Ca LSDCs. The results extracted by the forward-simulation analysis are shown in Fig. 3. The solubility Ca in Mg at 530 °C, 580 °C, 600 °C, and 630 °C is determined to be 0.44, 0.26, 0.22, and 0.08 at.% Ca, respectively (Note the extremely low value at 630 °C!). At such low solubility values, it is reasonable to assume that the interdiffusion coefficients are constant at each temperature and are equal to the impurity diffusion coefficients of Ca in Mg. The first ever set of impurity diffusion coefficients of Ca in Mg obtained from the present study can be represented by an Arrhenius equation $D_{Ca\ in\ Mg} = 0.06 \times 10^{-4} e^{-103700/RT}$ (in m²/s with T in Kelvin and $R = 8.314\ J\ K^{-1}\ mol^{-1}$), as shown by the solid red line in Fig. 3.

There are three first-principles studies on impurity/dilute diffusion coefficients in Mg [24–26]. Since Mg has an hcp crystal structure, the diffusion coefficients within the basal plane and that along the c-axis can be different in theory. First-principles calculations predicted slightly

different values as shown by two lines for each set of calculations. The computed results (dashed lines) are compared with the experimental results (symbols and the solid line) in Figs. 2(c) and 3(b). For the Al impurity diffusion coefficients in Mg, the first principles results from Ganeshan et al. [24] are significantly lower than the consentaneous experimental results while the computed results from Wu et al. [25] and Zhou et al. [26] are much closer, Fig. 2(c). The three sets of first-principles calculations of Ca impurity diffusion coefficients in Mg have mostly predicted higher values than our experimental measurements, Fig. 3(b). Interestingly, the first-principles calculations have predicted the activation energy (slope of the lines in Fig. 3(b)) reasonably well.

In the absence of experimental diffusion data, Ca has been often assumed to be a slow diffuser in Mg as rare earth elements. Our results, summarized in Fig. 4, clearly show that the Ca diffusion in Mg is significantly faster than the Mg self-diffusion which is faster than the Al diffusion in Mg. The fast Ca diffusion may come as a surprise to researchers who have assumed slow Ca diffusion in Mg in hope of achieving high creep strength in Ca-alloyed Mg alloys for high temperature applications.

In summary, a novel and simple liquid-solid diffusion couple (LSDC) geometry (Fig. 1) is designed and integrated with a recently developed forward-simulation analysis for effective study of Al and Ca diffusion in Mg. The newly developed approach enables us to obtain the impurity diffusion coefficient of Ca in Mg for the first time – no other experiments have been attempted or succeeded in obtaining such data since there is no suitable radioactive isotopes of Ca for tracer experiments and the extreme low solubility of Ca in Mg makes it very hard to make incremental solid-solid diffusion couples with the right dilute alloy compositions. This LSDC and forward-simulation analysis approach should be widely applicable to many alloy systems to evaluate diffusion coefficients at elevated temperatures, especially for numerous challenging low-eutectic binary systems and/or extreme low solubility solid solutions. In this study, reliable impurity and interdiffusion coefficients have been obtained at temperatures as high as 20 °C below the melting point of Mg with solubility as low as 0.08 at.%. The best judgement impurity diffusion coefficients of Ca and Al in Mg are recommended as two Arrhenius equations. Ca is found to diffuse faster than the Mg self-diffusion which is faster than the Al diffusion in Mg.

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Figure captions:

Fig. 1. Geometry of a liquid-solid diffusion (LSDC) couple: (a) Photo of a LSDC (~20 x 20 x 25 mm); (b) Schematic of a cross section; (c) Example of a LSDC after diffusion heat treatment showing its melted/liquid region after the sample was quenched to room temperature and sectioned; and (d) SEM image of the liquid-solid boundary of a Mg-Ca LSDC that was diffusion annealed at 630 °C for 13 h and then water quenched to room temperature. The solidified liquid phase pool is on the top and the solid-solution is at the bottom. The vertical line in the middle is the overlay of circles of some of the EPMA scan points.

Fig. 2. The Mg-Al LSDC results: (a) Experimental and simulated concentration profiles at four temperatures; (b) Interdiffusion coefficients as a function of the Al concentration for the hcp phase of the Mg-Al system obtained from this study in comparison with the results of Kammerer et al. [17]; and (c) Impurity diffusion coefficients of Al in Mg (Experimental results are shown as symbols and the first-principles calculations [24-26] are shown as dashed lines for comparison. The solid line represents the best-judgement assessment of experimental results. SIMS refers to secondary ion mass spectrometry and DC stands for diffusion couple).

Fig. 3. The Mg-Ca LSDC results: (a) Experimental and simulated concentration profiles at four temperatures with the details of the extreme low solubility values in the inset; and (b) Impurity diffusion coefficients of Ca in Mg as a function of temperature. The present experimental results are shown as symbols and the solid line, and the first-principles calculations [24-26] are shown as dashed lines for comparison.

Fig. 4. Comparison of the impurity diffusion coefficients of Ca and Al in Mg obtained from the present study with the self-diffusion coefficients of Mg within the basal plane (//) and along the c-axis (⊥) reported by Combronde and Brebec [27].

Figure1

Figure2

Figure3

Figure4