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



Wei Zhong, Ji-Cheng Zhao *

Department of Materials Science and Engineering, The Ohio State University, 2041 College Road, Columbus, OH 43210, USA

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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 impurity 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.

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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 at elevated temperatures and poor formability at room temperature [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 are available for several key alloying elements.

Experimentally measured interdiffusion and impurity 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 (dilute) 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 are used to assemble the LSDCs. All pieces are 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 × 20 × 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(b)) 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(b). A carbon steel screw is applied at the top to tighten the diffusion

* Corresponding author.

E-mail address: zhao.199@osu.edu (J.-C. Zhao).

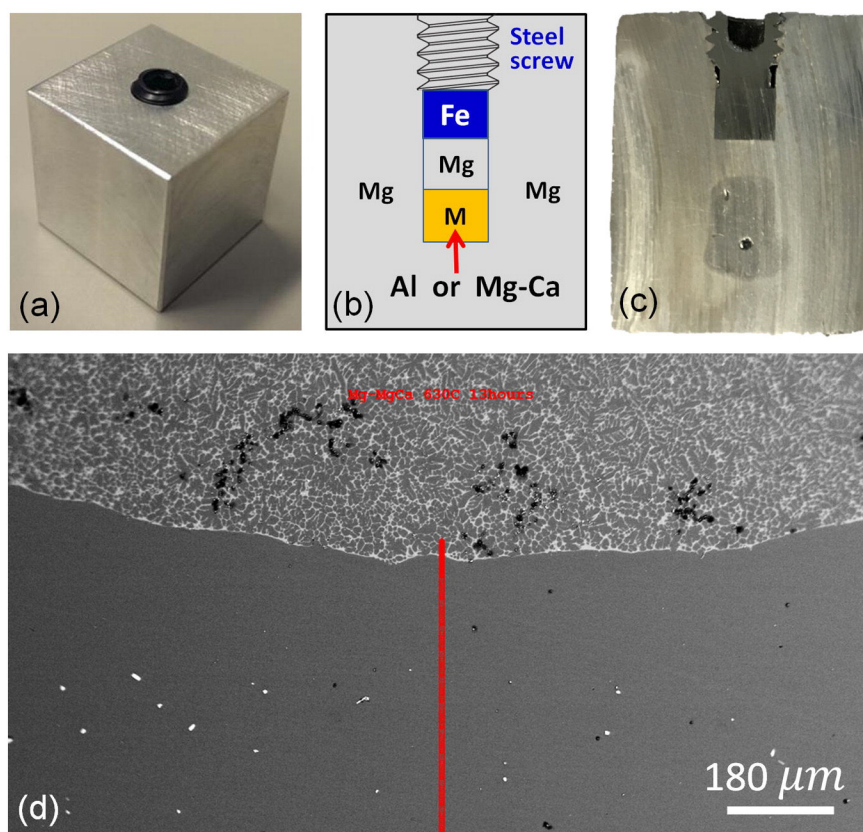


Fig. 1. Geometry of a liquid-solid diffusion (LSDC) couple: (a) Photo of a LSDC ($\sim 20 \times 20 \times 25$ mm); (b) Schematic of a cross section; (c) Example of a LSDC after diffusion heat treatment showing its melted/liquid region after the sample was quenched to room temperature and sectioned; 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.

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 $1/5$ atm 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. Fig. 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 are 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 are 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 are varied among samples, from $1\ \mu\text{m}$ to $5\ \mu\text{m}$ 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.

Fig. 2(a) shows the EPMA results of the Mg-Al LSDCs that are 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 compositions of the solidified liquid phase (compositions beyond (to the right of) the smooth single-phase Mg solid solution in Fig. 2(a)) show 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} m^2/s , it is safe to assume that the composition of the liquid phase is homogeneous at an annealing temperature above the eutectic point. An assumption is also made that the

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