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Development of Lightweight, Corrosion-Resistant Magnesium Alloys
Formable at Room Temperature
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FINAL REPORT

Background and Motivation

There is a need for lightweight structural materials for transportation to improve the performance and energy efficiency. Because magnesium (Mg) is 36% less dense than aluminum (Al) (1.74 g/cm³ for Mg vs. 2.70 g/cm³ for Al), Mg-based alloys have received increasing attention lately. The limiting property of Mg and its alloys at the present time is poor ductility (and formability) at room temperature; therefore the Mg alloys are used primarily in the cast or extruded condition. Development of Mg alloys with sufficient strength and enhanced ductility at ambient temperature will lead to significant energy savings (a) by replacing Al alloys with lighter Mg alloys in vehicles and (b) by being able to be formed into complex shapes at room temperature instead of 150-200°C (required for forming) or 650°C (required for casting or extrusion).

The goal of the project was to provide the basis for development of a new class of magnesium alloys that are formable at room temperature.

The poor ductility of Mg and its alloys at room temperature is due to its HCP (hexagonal close-packed) crystal structure, which provides only two independent slip systems for easy plastic deformation. These are on the basal plane. Homogenous deformation of polycrystalline metals requires five independent slip systems. Slip on the basal plane requires only a small stress to move a dislocation from one energy valley to the next (the Peierls stress). In contrast slip on the pyramidal or prismatic planes require a slip component in the c direction. These dislocations have very high Peierls stresses, the source of the very poor formability. Dislocations with high Peierls stress move by nucleating a double kink along their length followed by expansion of the double kink. Nucleation of a double kink requires high activation energy when the Peierls stress is high. The interaction between a dislocation and a small misfitting nanosize size precipitate locally reduces the activation energy needed to form a double kink increasing the dislocation’s mobility. A lower stress is then needed to nucleate a double kink increasing the formability at room temperature.

Our approach to find and develop a ductile Mg alloy has been to seek a precipitation hardening systems where such nano-sized coherent precipitates would form. We used this approach successfully in the past for design of fracture-tough steel at cryogenic temperature.[1] We have also demonstrated recently the applicability of this concept to Mg alloys by examining a specific region of the Mg-Li-Zn phase diagram, specifically Mg-2.4Li-5.1Zn (in wt.%; density 1.71 g/cm³). The alloy was cast for us by Sophisticated Alloys, Inc., followed by solution treatment and aging we devised. This alloy was shown to achieve remarkable formability; this alloy did not form cracks even when bent on itself 180° around a mandrel at room temperature.

In the present project we investigated two systems: (a) Mg-Ca-Zn ternary and (b) Mg-Li-Zn-Ca quaternary. We selected these systems for several reasons. First, Li is known to improve some ductility of Mg. Second, the two lower-order systems (Mg-Zn and Mg-Ca-Zn) are known to form nanometer-sized precipitates (GP zones) as result of solution treatment and aging at appropriate temperatures. These precipitates were expected to increase strength and enhance room-temperature ductility. Further, there is literature evidence that Ca improves the corrosion resistance of Mg alloys. In addition, the reduction of the amount of Zn in the alloy and substituting it with Ca should lead to further weight reduction and to improved corrosion resistance.

RESULTS AND DISCUSSION

Modeling of ternary Mg-Ca-Zn system

The computational work was focused on modeling phase stability of the Mg-Ca-Zn system. It is well known that dilute Mg-Zn alloys decompose by forming GP zones, while Ca reduces solubility of Zn in Mg. Reducing amount of Zn in the alloy is very desirable because Zn significantly increases the corrosion of Mg alloys. Due to limited funding the modeling of much more complex quaternary system (Mg-Li-Ca-Zn) was not performed.

Knowledge of phase equilibrium of the Mg-Ca-Zn system is rather sparse. So far, two ternary phases have been reported: (i) Ca₂Mg₅Zn₄ [2] but its crystallographic details are not known; (ii) Jardim et al [3] reported Ca₂Mg₂Zn₃ (having complex hexagonal structure) that formed during aging of a rapidly solidified Mg-Ca-Zn alloy.
Only the latter phase is considered in the present study.

A major problem with available experimental phase diagrams, due to limited experimental information, is that the solution treatment temperature of Mg due to additions of Ca and Zn cannot be predicted by extrapolation and/or interpolation and the state of alloys during aging at lower temperature cannot be predicted. To bridge these important knowledge gaps, we have employed modern computational approach of Calphad [4] in conjunction with appropriate tools.

We have performed extensive and systematic ab initio calculations using total energy and electronic structure code VASP (Vienna Ab Initio Simulation Package) and ATAT (Alloy Theoretic Automated Toolkit) code [5,6]. Heat of mixing of solid solutions was calculated using ATAT code [7,8] that interfaces with VASP and employs cluster expansion technique. Relevant ternary phase diagrams were calculated using Thermo-Calc software [9]. For this purpose, a thermodynamic database was created using relevant parameters available in published literature. Specifically, parameters for the Ca-Mg and Mg-Zn systems are taken from References 10 and 11, respectively, while those of the Ca-Zn system are taken from Brubaker and Liu [12]. Several ternary interaction parameters were also needed, and they were adopted from the work of Brubaker and Liu [13].

Figure 1 shows calculated polythermal section of Mg-0.6 wt.%Ca-0.9 wt.%Zn alloy. This diagram suggests the use of solution temperature of 450°C or higher for this alloy to bring all elements into a single phase. Also, three aging temperatures are suggested; at 150°C three phases are present (Mg, Ca2Mg6Zn3 and CaMg2), at 180 and 200°C two phases are present (Mg, CaMg2). These temperatures were used in our investigation of Mg-Ca-Zn alloy.

**Experiments with Mg-0.6 wt.%Ca-0.9wt.% Zn alloy**

Alloy was melted and cast into 4” wide, ½-inch thick, 6-inch high mold by Sophisticated Alloys, Inc. At Northwestern University the alloy was solutionized at 450-460°C for 4 hours in argon atmosphere in a vertical tube furnace in attempt to dissolve precipitates in the Mg matrix. Then the specimen was water quenched. The microstructure was revealed by etching of polished specimen in mixture of 50 ml water, 150 mm ethanol and 1 ml of acetic glacial acid for 60 seconds with agitation.

Figure 2 shows the alloy in as-received (2a) and in solutionized (2b) conditions at the same magnification, 1000X. It is obvious that the alloy in both conditions has a lot of voids and contains precipitates. The grain size of alloy increases significantly during the 4 hours solutionizing but the precipitation in the grain boundaries is still significant.

The aging studies were performed at 150, 180 and 200°C in air. The hardness was measured by Duramin hardness tester with a load of 50 grams. The average of 10 measurements is plotted for each data point in Figure 3. It is evident that the alloy ages significantly (about 30%) at all aging three temperatures indicating formation of the strengthening precipitates in the matrix.

To quickly determine the room-temperature formability of Mg-0.6 wt.% Ca-0.9 wt.% Zn alloy, the rectangular specimens (50 mm long, 12 mm wide and 1-1.5 mm thick) were cut, polished and then manually bent around a mandrel (5mm in diameter). We tested the room-temperature formability of the alloy solutionized for 4 hours in argon at 450-470°C and water-quenched and also solutionized, water quenched and then aged in argon for approximately 15 min at 190-200°C. The aged alloy was brittle; numerous cracks were formed and specimen could not be bent around the mandrel. The as-quenched specimen was remarkably ductile; despite numerous voids and precipitates along grain boundaries no cracks were formed in the specimen bent around mandrel at room temperature (Figure 4). 3D Atom Probe (3DAP) Tomography was employed to find small precipitates that could form during “slow” water quench or aging of this alloy. Two specimens were investigated. In water quenched
specimens no Zn-Ca precipitates were detected. In a specimen that was aged in argon for approximately 15 min at 190-200°C only large precipitate (appr. 20 nm in diameter) was found (Figure 5a). The precipitate core composition was approximately Mg-8at.%Zn-3.5at.%Ca, averaged from the plateau in the proxigram, Figure 5b. The proxigram was calculated with respect to a 3at.% Zn isoconcentration surface. Please note that the proxigram goes only up to 6 nm distance into the precipitate since the precipitate is cut by the surface of the reconstruction and only partially captured.

Due to few reasons it was not unexpected not to find smaller precipitates. First, it is extremely difficult to do 3DAP Tomography of Mg alloys due to their very high electrochemical activity. Second, the small precipitates that are formed in Mg alloys during cooling from solutionizing temperature transform very fast into very thin plates that are difficult to detect by 3DAP Tomography[14]. High resolution transmission electron microscopy (HRTEM) probably is better way to detect these precipitates. However, the use of HRTEM due to funding limitations was out of scope of this project. The use of these analytical techniques to detect the precipitates in Mg alloys will be proposed for future work.

Experiments with Mg-2.2wt.%Li-0.60wt.%Ca-0.90wt.%Zn alloy

The quaternary Mg-Li-Ca-Zn we studied contained the same amount of Ca and Zn as the ternary alloy and 2.2wt.%Li was added. This amount of Li was used by us in the prior research of Mg-Li-Zn alloy. It was found then that when underaged the Mg-Li-Zn alloy is very ductile at room temperature.

The melting, heat-treatment and microstructural analysis of quaternary Mg-2.2wt.%Li-0.60wt.%Ca-0.90wt.%Zn alloy was similar to that of ternary Mg-0.60wt.%Ca-0.90wt.%Zn alloy (described above).

The optical micrograph (Figure 6) of the solutionized and water-quenched alloy shows that it contains similarly to a ternary alloy a lot of voids and inclusions. This was expected since it was produced by simple melting of the elements and casting in vacuum. The production of a cleaner and void-free alloy requires much more very expensive processing.
Similarly to ternary alloy the formability of quaternary alloy was tested by bending specimens manually around a mandrel (5mm in diameter). We tested the room-temperature formability of the alloy solutionized for 4 hours in argon at 450-470°C and water-quenched and also as solutionized, water quenched and then aged in argon for approximately 15 min at 190-200°C. The results are shown in Figure 7. It is obvious that alloy that was only quenched is formable at room temperature (i.e. does not crack when bent around mandrel) while the aged specimen is brittle (i.e. breaks during bending). It is important to stress that an alloy that has numerous defects could be formed easily at room temperature after appropriate heat treatment.

SUMMARY

High room-temperature formability of ternary (Mg-0.60wt.%Ca-0.90wt.%Zn) and quaternary (Mg-2.2wt.%Li-0.60wt.%Ca-0.90wt.%Zn) alloys was demonstrated when appropriately heat-treated. The good formability is assumed to be result of formation of nan-sized precipitates in the matrix that interact with dislocation and increase the dislocation’s mobility. However, no nano-sized precipitates were detected by 3DAP tomography in Mg-0.60wt.%Ca-0.90wt.%Zn alloy. Further work that might involve HRTEM would be required to detect these precipitates.

FURTHER WORK

The experimental results generated during performance of this project were part of the patent application filed by Northwestern University in December 2014.

The funding to continue this work is sought at NSF, US Air Force, DARPA, DOE, and few companies through McCormick School of Engineering and Applied Science Office for Corporate Relations.

REFERENCES