Magnesium Technology 2012
Edited by: Suveen N. Mathaudhu, Wim H. Sillekens, Neale R. Neelameggham, and Norbert Hort
TMS (The Minerals, Metals & Materials Society), 2012

PRECIPITATION BEHAVIOUR OF MICRO-ALLOYED MG-AL-CA ALLOYS DURING HEAT TREATMENT AND HOT COMPRESSION

Jing Su, Shirin Kaboli, Abu Syed Humaun Kabir, Phuong Vo, In-Ho Jung and Stephen Yue

Department of Mining and Materials Engineering, McGill University, Montreal, Canada

Key words: Mg-Al-Ca, precipitation, heat treatment and hot compression

Abstract

Based on thermodynamic calculations, two micro-alloyed Mg-Al-Ca alloys, Mg-0.3Al-0.2Ca and Mg-0.1Al-0.5Ca, were selected in terms of the equilibrium precipitation temperatures of Al_2Ca and Mg_2Ca, respectively. The basic idea is to form precipitates during hot compression to examine their effect on hot deformation. Both alloys, cast by copper mould, were solution treated at 500°C for 8 hours to dissolve eutectic precipitates which formed in the as-cast microstructure, and then isothermally heat treated at 350°C for different times. SEM analysis of the heat treated alloys generally agreed with thermodynamic calculations. Hot compression tests were also conducted on solution treated alloys at 350°C with a strain rate of $0.01s^{-1}$ and different strains (10%, 30%, 60%, and 90%). The precipitation behaviour and microstructural evolution which was characterized by optical microscopy and SEM with BSE and EDS detectors during isothermal heat treatment and hot compression were compared.

Introduction

Recently Mg alloys have drawn great attention as structural materials for automotive application due to their low density, high strength to weight ratio and high stiffness to weight ratio compared with steel and aluminium. However, due to the poor formability of Mg alloy sheets, the development of new alloys is required for future application [1,2]. It is known that the addition of calcium to magnesium is effective in grain refinement during casting [3-7] as well as improve oxidation resistance, increase ignition temperature and improve creep resistance [7,8]. Furthermore, calcium is cheaper and has lower density ($1.55g/cm^3$) than rare-earth elements (Neodymium, yttrium, thorium etc.) which are now being considered to weaken texture [10-13]. Aluminium is regarded as a strengthening element due to forming solid solution with magnesium and a significant difference of the atomic diameter with magnesium [14]. As well, Mg–Al–Ca system alloys are also considered due to their good castability [9].

Previous studies have reported that Mg-Al-Ca alloys have high strength at elevated temperature due to formation of thermally stable intermetallic compounds Al_2Ca, Mg_2Ca or $(Mg,Al)_2Ca$ [8,15,16]. In comparison with the $Mg_{17}Al_{12}$ phase, Mg_2Ca and Al_2Ca phases have higher melting points (460°C for $Mg_{17}Al_{12}$, 715°C for Mg_2Ca and 1079°C for Al_2Ca) and thus, are relatively stable at elevated temperatures [17]. An increase in the Ca content results in a reduction of the $Mg_{17}Al_{12}$ phase as well as the formation of thermally stable secondary phases containing Ca [5]. However, these precipitates in magnesium alloys tend to be coarse and brittle [18]. Therefore, workability is rather poor due to the tendency of de-bonding from the magnesium matrix during plastic deformation. Both decreasing the grain size and refining the coarse compounds into small precipitates can improve the formability during plastic working [8].

In addition, precipitates can be used to modify the texture and control grain size during thermal-mechanical processing. Particles may either promote or retard recrystallization depending on their size, spacing and fraction [19]. It has been shown in some prior investigations of magnesium alloys that the change in texture was a result of the operation of PSN in systems containing particles larger than 1μm [12].

In this work, two Mg-Al-Ca alloys were chosen on the basis of forming high temperature precipitates during hot deformation. The effect of precipitates on hardening during isothermal heat treatment and dynamic precipitation during hot deformation were investigated.

Experimental Procedures

Materials and Casting Conditions

Two Mg-Al-Ca alloys were prepared using 99.9% pure Mg, 99.9% pure Al and Mg-30% Ca master alloy. The pure magnesium was melted in a graphite crucible using a high-frequency induction furnace at 690°C. Pure Al and Mg–30wt.% Ca master alloy were then added to the melt at 700°C and held for 15min to dissolve. The molten metal was cast under an SF_6 and CO_2 gas mixture atmosphere from 730°C into a preheated cylindrical copper mould to obtain billets of 15mm in diameter and 145mm in length.

Heat Treatment and Hardness Test

The as-cast specimens were homogenized at 500°C for 8 hours and quenched in water to dissolve all eutectic precipitates and obtain a supersaturated solid solution. They were then isothermally heat-treated at 350°C for periods ranging from 10min to 32 hours. Hardness tests were conducted by using a Clark CM-100AT micro-hardness tester and a load of 50gf with a minimum of ten measurements for each specimen.

Compression Test

Compression specimens were machined from the solution heat-treated bars into cylinders with a length of 11.4mm and a diameter of 7.6mm (a ratio of 1.5). Hot compression tests were conducted using a 100kN MTS servo-hydraulic testing machine at 350°C with a strain rate of $0.01s^{-1}$ and strains from 10% to 90%. The specimens were heated to the deformation temperature and held for 10min prior to compression in order to ensure a uniform temperature along the specimen. During the test, the specimen was protected under an argon gas atmosphere to avoid oxidation while a combination of boron nitride powder on mica was used to minimize friction between the anvil and specimen. The specimens were quenched within 2 seconds after compression to freeze the deformed microstructure.

Microstructure Characterization

Samples were ground with SiC papers (from No.400, No.600, No.800 to No.1200), and then polished with 3μm and 1μm diamond suspension, and 0.05μm alumina powder. Picric–acetic solution (6g picric acid, 15ml acetic acid, 10ml H_2O and 100ml ethanol) and 2% Nital solution were used to etch samples. Optical microscopy (Nikon EPIPHOT 200) and SEM (Philips XL30 and Hitachi SU8000) with backscattered electron detector (BSE) was used to characterize the microstructure while energy dispersive spectroscopy (EDS) was used to identify composition of the second phase.

Results and Discussion

Thermodynamic Calculations and Alloys Design

The design purpose of this study is to form thermally stable precipitates either during hot deformation or annealing after deformation, which may influence recrystallization behaviour and texture evolution depending on the size and distribution of precipitates. In this study, 350°C was chosen to be the deformation temperature for Mg-Al-Ca alloys, as the expected industrial hot deformation temperature range for Mg alloys is between 300°C to 400°C. The criterion for selecting alloy composition was the presence of a second phase (Al_2Ca or Mg_2Ca) at 350°C without $Mg_{17}Al_{12}$ phase. According to the ternary phase diagram of Mg-Al-Ca alloy at the Mg corner at 350°C (Fig.1) calculated from FactSage software with FTlite database, additions of less than 0.8% Al do not form $Mg_{17}Al_{12}$ phase. The composition of the alloys in the present study was determined based on the calculated Mg-Al-Ca equilibrium phase diagram at 350°C (Fig.2). The selected alloys of Mg-0.3Al-0.2Ca (alloy 1) and Mg-0.1Al-0.5Ca (alloy 2) feature a Mg matrix with single second phases of Al_2Ca (laves 15) and Mg_2Ca (laves 14), respectively.

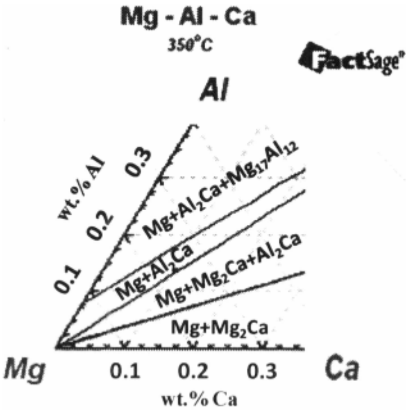


Fig.1 Ternary phase diagram of Mg-Al-Ca alloy at Mg corner at 350°C calculated from Factsage software with FTlite database

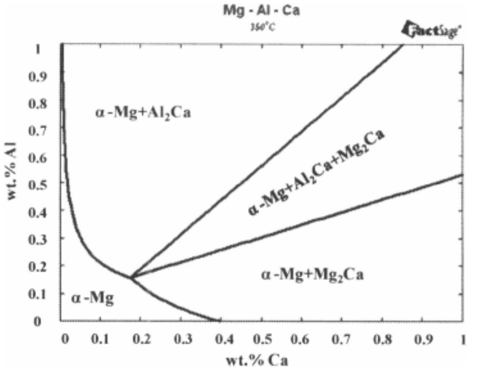
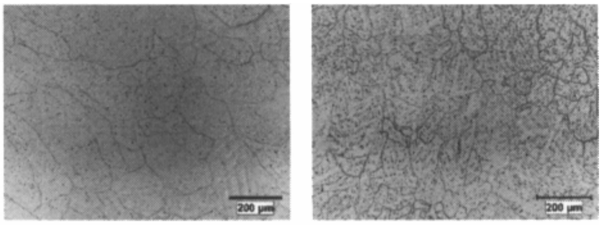


Fig.2 Isothermal phase diagram of Mg-Al-Ca alloy at 350°C calculated from FactSage software with FTlite database

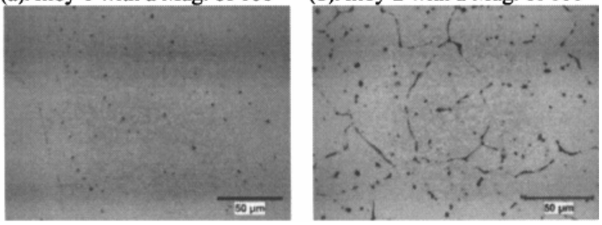
As-cast Microstructure

The optical microstructures of as-cast alloy 1 and 2 are shown in Figure 3. As shown at low magnification (Fig.3 (a),(b)), the grain size of alloy 1 was slightly larger than that of alloy 2. The finer microstructure with increasing Ca level is consistent with previous studies [3-7]. The amount and size of precipitates in alloy 2 was larger than that in alloy 1, as shown at higher magnification in Fig.3(c),(d) The precipitates in alloy 2 were irregular in shape and tended to locate along grain boundaries and grain interiors, while precipitates were almost round in alloy 1 and preferentially distributed inside grains.

With closer analysis by SEM (Fig. 4), the precipitates in both alloys were observed to have a eutectic structure with Mg, Al and Ca peaks shown in the EDS spectrum. In the study of Suzuki et al. [20], the eutectic region was examined by TEM and reported to consist of a-Mg and a ternary compound of $(Mg,Al)_2Ca$ with dihexagonal C36 structure. Besides, there was a small amount of inclusions randomly dispersed in the as-cast microstructure of both alloys. These inclusions were faceted and around 500nm in size with impurity elements of Fe identified from EDS analysis.

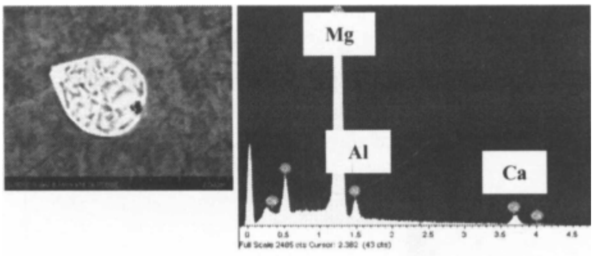


(a)Alloy 1 with a Mag. of 100 (b)Alloy 2 with a Mag. of 100



(c)Alloy 1 with a Mag. of 500 (d)Alloy 2 with a Mag. of 500

Fig.3 Optical microstructure of as-cast alloy 1 and alloy 2 with magnifications of 100 and 500

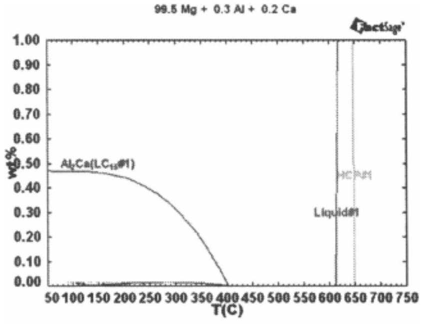


(a) (b)

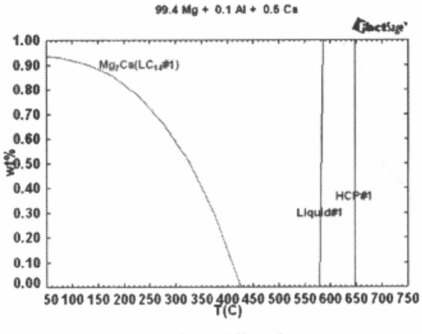
Fig.4 BSE image (a) and EDS spectrum of eutectic precipitate

Microstructure of Solution Heat Treated Alloys

From FactSage calculations (Figs. 5(a) and (b)), the solution heat treatment temperature ranges are above 400°C for alloy 1 and 430°C for alloy 2. It was found that after heat treatment at 500°C for 8h, eutectic precipitates formed in the as-cast samples were dissolved into the matrix. However, faceted inclusions consisting of Fe still remained, as shown in Fig. 6. The hardness values of alloy 1 and alloy 2 after solution heat treatment were approximately 40HV and 46HV, respectively, which was similar to the hardness of as-cast samples. The grain size of alloy 1 and 2 after solution heat treatment are approximately 190um and 200um, respectively.



(a) Alloy 1



(b) Alloy 2

Fig. 5 Equilibrium phase distribution of alloy 1 (Mg-0.3Al-0.2Ca) (a) and alloy 2 (Mg-0.1Al-0.5Ca) (b)

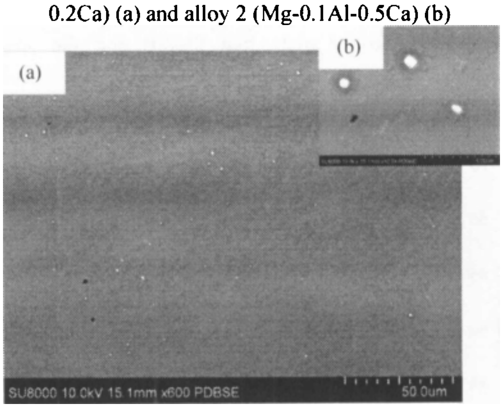


Fig.6 BSE images of solution heat treated alloy 2 with (a) a Mag. of 600 and (b) a Mag. of 10000

Microstructure and Hardness During Isothermal Heat Treatment

In Fig.7, the hardness curves of alloy 1 and alloy 2, which were isothermally heat-treated at 350°C from 10 min to 32 hours after solution heat treatment, were shown. In general, the hardness of alloy 2 is higher than that of alloy 1 for all times of the 350°C heat treatment. This results from larger number of precipitates and slightly smaller grain size of alloy 2 than that of alloy 1. Concerning of the solution hardening effect of aluminium on these two alloys, alloy 1 was added larger amount of aluminium than that of alloy2, which may compensate for the hardness of alloy 1 a little bit.

The variation of hardness value of alloy 1 and alloy 2 were both very small along all time range. The precipitates had already formed at 10min heat treatment and the amount of precipitates increased with time (Figs.11 (a) and (b)), but there is no obvious increase of hardness value (only 1 to 2 HV). There are two possible reasons. First, the volume fraction of precipitates in both alloys was too small, even at longer times. Second, this is because of the morphology of precipitates or the crystallographic relationship between precipitates and matrix of precipitates, since precipitates prefer to grow along the basal plane of magnesium alloys, which is ineffective to inhibit the basal slip and hardening the alloys [18, 20]. The slight decrease of hardness in alloy 2 was mainly due to coarsening of precipitates, as seen from Fig. 8 (a) and (b), as there is no apparent grain growth. The hardness of both alloys from 8 hours to 32 hours was more or less constant. This suggests that the grain boundary precipitates inhibit grain coarsening.

From the FactSage simulation (Figs.5 (a) and (b)) in the equilibrium condition, the amount of second phase in alloy 2 is approximately double that of alloy 1 (about 0.4 wt.% vs 0.2wt.% at 350°C). This level of difference is supported by BSE images (for example, alloy 1 and alloy 2 heated for 4 hours shown in Fig. 9). As well, EDS spectrums of precipitates in alloy 1 and alloy 2 were shown in Fig. 10. Mg, Al and Ca peaks were shown in alloy 1, while only Mg and Ca peaks appeared in alloy 2. According to the EDS spectrum (Fig.10) and the FactSage simulation, the precipitates in alloy 1 and alloy 2 were Al_2Ca and Mg_2Ca, respectively. The precipitates in both alloys are oval (disk-like or plate like [7,20]) and the size of precipitates in alloy 1 is smaller than that in alloy 2 at same heat treatment time.

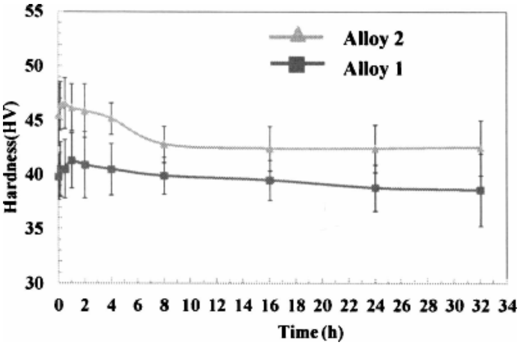
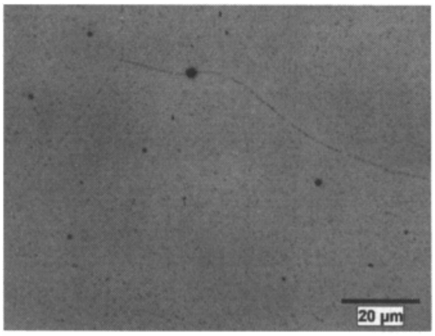
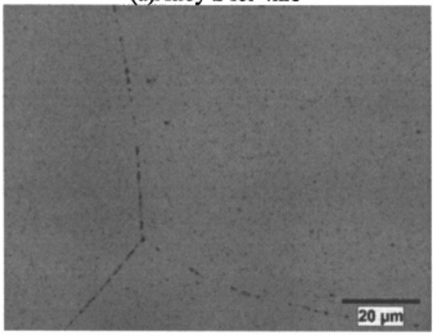


Fig.7 The hardness curves of alloy 1 and alloy 2 at 350°C from 10 min to 32 hours

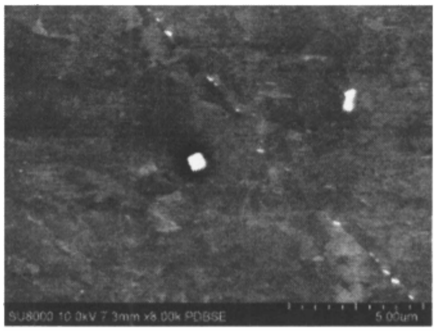


(a)Alloy 2 for 4hrs

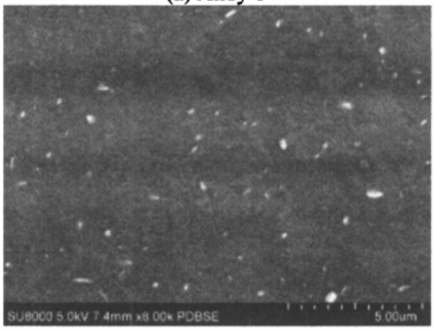


(b)Alloy 2 for 8hrs

Fig. 8 Optical microstructure of alloy 2 heated at 350°C for 4 hours(a) and 8 hours(b) with a Mag. of 1000

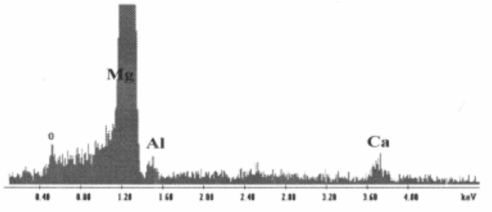


(a) Alloy 1

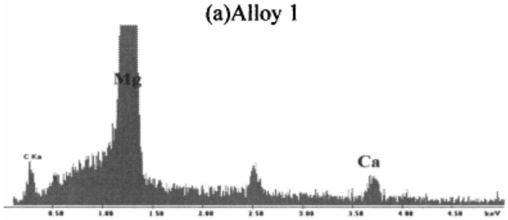


(b) Alloy 2

Fig. 9 BSE images of alloy 1 and alloy 2 isothermally heat treated at 350°C for 4 hours



(a)Alloy 1

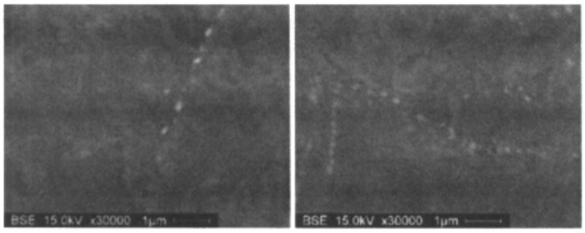


(b)Alloy 2

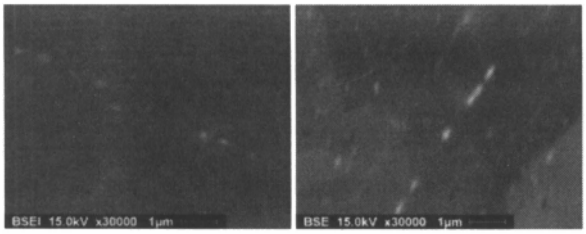
Fig.10 Spectrum of precipiates of alloy1 (a) and alloy 2 (b) during heat treatment at 350°C by EDS

Microstructure evolution during hot compression

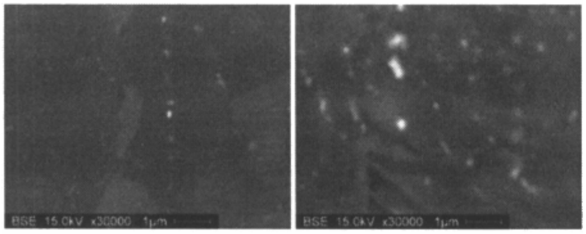
Specimens at 10min heat-treated condition were characterized, since they have to be kept at deformation temperature for 10min prior to compression to achieve uniform temperature. After a 10min heat treatment at 350°C in alloy 1, a small number of precipitates formed along grain boundaries, as shown in Fig. 11(a). After deformation at 350°C and a strain rate of $0.01s^{-1}$, the amount of precipitates did not significantly changed at 10% and 30% strain (Fig.11(c)) and slightly increased at 60% to 90% strain (Fig.11(e)). In alloy 2, the variation in precipitates level was small at low strains (Fig.11(d)) compared with the heat treated sample (Fig.11(b)) and displayed a clear increase in the 60% and 90% strained samples (Fig.11(f)). Therefore, strain induced precipitation occurred in both alloys. However, alloy 2 has more obvious enhancement of precipitation with increase of strain. For 10mins heat treatment without deformation and with deformation at 350°C, more precipitates formed in alloy 2 compared with alloy 1. The sizes of precipitates forming in alloy 1 and alloy 2 are both around 200nm and there is no apparent coarsening of precipitates with increasing of strains. From the recrystallization point of view, alloy 2 is expected to have more effect on dynamic or static recrystallization behaviour [19], since more precipitates form in alloy 2 during hot compression. The relationship of dynamic recrystallization and precipitation behaviour will be done in the future work.



(a)Al 10min heat treatment (b) A2 10 min heat treatment



(c) A1 with a strain of 30% (d) A2 with a strain of 30%



(e) A1 with a strain of 60% (f) A2 with a strain of 60%

Fig.11 BSE image of alloy 1 and alloy 2 heat treated for 10mins(a)(b) and compressed at 350°C with a strain rate of $0.01s^{-1}$ and strains from 30%(c)(d) and 60%(e)(f)

The flow curves of alloy 1 and alloy 2 were shown in Fig. 12. Below 20% deformation, alloy 2 had higher strength than alloy 1. The top stress values for alloy 1 and alloy 2 were both around 52MPa at a strain of 40%. And the softening behaviour of two alloys was similar at larger stains (60% to 90%). The hardness of both alloys went up with increasing strains, as shown in Fig. 13, which is partly due to precipitation induced by strains. As similar as isothermal heat treatment, the hardness of alloy 2 was higher than that of alloy 1 at all strains. In addition, hardening effect on compressed samples was more efficient compared with that on heat-treated ones. The possible reasons include work hardening effect as well as a large amount of small size and dispersed precipitates in deformed specimens.

During hot compression, the amount of precipitates increases with increasing strains. This is mainly related to more nucleation of precipitates, since more nucleation sites, such as dislocations, deformation bands or sub-grain boundaries, caused by deformation. Compared with the dynamic precipitates during deformation, the volume fraction of precipitates increases with time during isothermal heat treatment, which is primarily because of growth of precipitates.

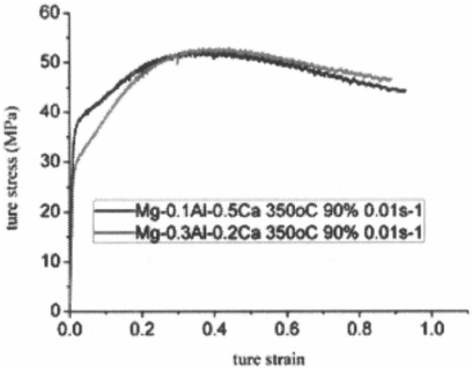


Fig. 12 Flow curves of alloy 1 and alloy 2 compressed at 350°C with a strain rate $0.01s^{-1}$ and a strain of 90%

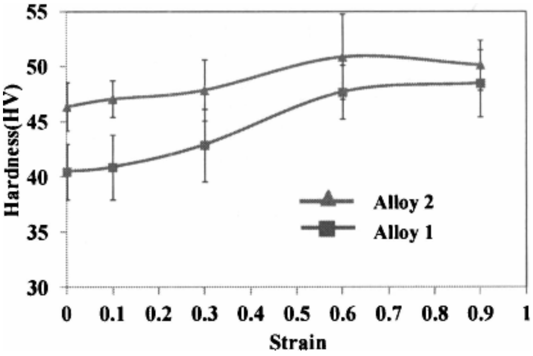


Fig.13 The hardness curves of alloy 1 and alloy 2 compressed at 350°C with a strain rate of $0.01\ s^{-1}$ and stains of 10%, 30%, 60% and 90%

Summary

(1) In the as-cast microstructure, a-Mg and eutectic (Mg,Al)$_2$Ca precipitates formed in both alloys, which can be dissolved into matrix at 500°C for 8 hours heat treatment.

(2) During isothermally heat treatment at 350°C, Al$_2$Ca phase formed in alloy 1, while Mg$_2$Ca formed in alloy 2. Larger amount of precipitates formed in alloy 2 than that in alloy 1, which resulted in higher hardness value of alloy 2. And the hardness of both alloys didn't apparently drop even for 32 hours due to the precipitates pinning on the grain boundaries.

(3) During hot compression at 350°C with a strain rate of $0.01s^{-1}$, strain induced precipitation more obviously occurred in alloy 2 compared with alloy 1. And the hardness of both compressed alloys increased with strains.

(4) Increase of volume fraction of precipitates during heat treatment is due to precipitates growth, while during hot compression it relies on enhancing nucleation of precipitates.

Acknowledgement

This work was support by General Motor and NSERC, Canada.

Reference

1. B.L. Mordike, and T. Ebert, "Magnesium: Properties-Applications-Potential," *Materials Science and Engineering A,* 302 (1) (2001), 37-45.
2. R. VanFleteren. "Magnesium for Automotive Applications," *Advanced Materials and Processes,* 149 (5) (1996), 33-34.
3. L. Han, H. Hu, and D.O. Northwood, "Effect of Ca Additions on Microstructure and Microhardness of an as-Cast Mg-5.0 wt.% Al Alloy," *Materials Letters* 62(3) (2008), 381-384.
4. B. Kondori, and R. Mahmudi, "Effect of Ca Additions on the Microstructure, Thermal Stability and Mechanical Properties of a Cast Am60 Magnesium Alloy," *Materials Science and Engineering A,* 527 (7-8) (2010): 2014-2021.
5. P. Li, B. Tang, and E.G. Kandalova, "Microstructure and Properties of AZ91D Alloy with Ca Additions," *Materials Letters* 59 (6) (2005), 671-675.
6. L. Shang, et al., "Effect of Microalloying with Calcium on the Microstructure and Hot Working Behavior of AZ31 Magnesium Alloy," *TMS 2007.*
7. J.F. Nie, B.C. Muddle, "Precipitation Hardening of Mg-Ca(-Zn) Alloys, " *Scripta Materialia,* 37 (1997), 1475-1481.
8. W.J. Kim, et al., "Microstructure and Superplasticity of Mg-Al-Ca Electromagnetic Casting Alloys after Hot Extrusion," *Materials Science and Engineering A,* 494 (2008), 391-396.
9. S. W. Xu, et al, "High Temperature Tensile Properties of as-Cast Mg-Al-Ca Alloys." *Materials Science and Engineering A,* 509 (1-2) (2009), 105-110.
10. J.W.Senn, and S.R.Agnew, "Texture Randomization of Magnesium Alloys Containning Rare Earth Elements, " *TMS* 2008.
11. T. Laser, et al., "The Influence of Calcium and Rare Earth Metals on the Microstructure and Mechanical Properties of Mg-3al-1zn During Extrusion, " *TMS* 2008.
12. J.D. Robson, D.T. Henry, and B. Davis, "Particle Effects on Recrystallization in Magnesium–Manganese Alloys: Particle-Stimulated Nucleation," *Acta Materialia,* 57 (2009), 2739-2747.
13. N. Stanford, and M. Barnett, "Effect of Composition on the Texture and Deformation Behaviour of Wrought Mg Alloys," *Scripta Materialia,* 58 (2008), 179-182.
14. K.P. Rao, et al., "Effect of Aluminum Addition on the Strengthening and High Temperature Deformation Behavior of Mg-3Sn-2Ca Alloy, " *TMS 2010.*
15. L.L. Rokhlin, and N.I. Nikitina, "Effect of Calcium on the Properties of the Mg-Al System," *Matal Science and Heat treatment,* 45 (2003), 171-173.
16. H. Watanabe, et al., "Mechanical Properties of Mg–Al–Ca Alloy Processed by Hot Extrusion," *Materials Science and Engineering A,* 454-455 (2007), 384-388.
17. L.L. Rokhlin, N.I. Nikitina, and V. A. Volchenkova. "Magnesium-Rich Mg–Al_2ca Alloys," *Russian Metallurgy (Metally,)* 2 (2006), 185-188.
18. B. Langelier, and S. Esmaeili, "The Effect of Zn Additions on Precipitation Hardening of Mg-Ca Alloys," *TMS 2010.*
19. F.J. Humphreys, *Recrystallization and Related Annealing Phenomena / F.J. Humphreys and M. Hatherly,* (Oxford, U.K. : Pergamon, 1995).
20. A. Suzuki, et al., "Precipitation Strengthening of a Mg-Al-Ca–Based AXJ530 Die-Cast Alloy," *METALLURGICAL AND MATERIALS TRANSACTIONS A,* 39A (2008), 696-702.