



EFFECT OF YTTRIUM ADDITION ON MICROSTRUCTURE AND HARDNESS OF CAST ZRE1 MAGNESIUM ALLOY

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ABSTRACT

In this research, optical observations, X- ray diffraction and hardness measurements were used to investigate the effects of yttrium (Y) additions on as cast ZRE1 magnesium alloy. 0.75 wt.% Y was added and compared with the base alloy. The microstructure results show the refinement of the grain by the addition of Y and the grains became smaller about 32 %, which led to the increment of hardness from 50 HV (as-cast ZRE1) to 56.6 HV (as-cast ZRE1+0.75 Y). Energy dispersive spectroscopy (EDS) results showed that the base alloy mainly contained α -Mg matrix and Mg-Zn-Ce as a second phase crystallized along the grain boundaries and with the addition of Y, Mg-Zn-Y-Ce phase was found as a new second phase, where Y combined with the original second phase, which confirmed by the X-ray diffraction (XRD) results and also there is no other phases was formed by the Y addition.

Keywords: magnesium, yttrium, microstructure, hardness.

INTRODUCTION

Magnesium and magnesium alloys are used in a wide variety of structural and nonstructural applications, due to they are light-weight, exhibit good strength and stiffness at both room and elevated temperatures and have high strength-to-weight ratios (tensile strength/density), comparable to those of other structural metals. Structural applications include automotive, industrial, materials-handling, commercial, and aerospace equipment. Magnesium alloys are also valuable for aerospace applications. Magnesium has relatively good electrical conductivity and thermal conductivity values. It also has a very high damping capacity, that is, the ability to absorb elastic vibrations (Davis 2009). Rare earths (RE) are recognized as a group of elements of the periodic table with unique chemical properties and extremely important for science, and their application was made difficult due to their extremely low concentrations in nature (Castor and Hedrick 2006). RE are added to magnesium alloys to improve the high temperature strength and creep resistance. They are usually added as mischmetal (MM) or didymium (Dm). Mischmetal is a natural mixture of the rare earths containing about 50 wt% cerium (Ce), with the remainder being principally comprised of lanthanum (La) and neodymium (Nd), and didymium is a natural mixture of approximately 85% neodymium (Nd) and 15% praseodymium (Pr). Addition of rare earth also reduces weld cracking and porosity in casting, because they narrow the freezing range of the alloys (Friedrich and Mordike 2006), (Davis 2001). Recently, developed alloys have contained separate rare earths. The properties of Mg-RE alloys are enhanced by the addition of zirconium to refine grain size and the strength is further increased, if zinc is added as well.

Higher creep strength at temperatures up to 250 °C have been achieved in the alloy ZRE1 (EZ33) (Ferro, Saccone *et al.*, 2013). ELEKTRON ZRE1 is a magnesium-base casting alloy, which combines excellent creep resistance up to 250 °C, with good room temperature

properties. It is completely free from micro-porosity and suitable for applications requiring pressure tightness. Elektron ZRE1 (EZ33) is used in aero engine components where improved creep resistance is required. In the aero-engine industry, magnesium alloys are being used successfully in both civil and military aircrafts. Civil applications include intermediate casings for the engines and gearboxes & also in military aircraft, including the F16, Tornado and Eurofighter Typhoon, which capitalize on the lightweight characteristics of magnesium alloys for transmission casings (Friedrich and Mordike 2006).

(Rzychoń, Szala *et al.*, 2012) reported that as-cast microstructure of ZRE1 magnesium alloy consists of α -Mg matrix and (Mg, Zn)₁₂RE phase at the grain boundaries. The (Mg, Zn)₁₂RE compound exhibited high stability of the chemical composition and morphology at temperature 150°C for 1000h. At 200°C, the first stages of spheroidizing of the (Mg, Zn)₁₂RE are observed, therefore the hardness of the ZRE1 alloy is slightly lower than that in the alloy annealed at 150°C. In addition, the degradation of the microstructure of the ZRE1 alloy at 400°C was inducing by low oxidation resistance. This effect causes the formation of the porous MgO layer and the oxidation of the (Mg, Zn)₁₂RE compound. Thus the mechanical properties of ZRE1 magnesium alloy decreased after heated at 200 °C, and cannot be heat treated the alloy above 400 °C. They also found that the alloy poured from 730°C shows the highest UTS and hardness compared with the alloys poured from 780 °C and 830 °C (Rzychoń, Szala *et al.* 2012). Yttrium has a relatively high solid solubility in magnesium (12.4 wt%), and is added with other rare earth elements to promote creep resistance at temperatures up to 300 °C (Dobrzański, Król *et al.*, 2010). (Xu, Tang *et al.*, 2007) studied the influence of Y on the mechanical properties of the as-cast Mg-5.5Zn-xY-0.8Zr alloys (with element Y content of 0, 1.08, 1.97 and 3.08 wt.%). They found that the alloy with Y content of 1.08 wt.% had the best tensile strength, but its ductility was the lowest. When Y content reached 1.97 or 3.08 wt.%, the



tensile strength of the alloys significantly decreased, but the ductility had a little improvement. The linearly intercepted grain sizes of base alloy and with Y additions alloy of 1.08, 1.97 and 3.08 wt.% are 190, 130, 95 and 65 μm , respectively. It shows that with the increase of Y additions, the grain sizes of the as-cast Mg–Zn–Y–Zr alloys significantly decreased. X-ray results showed that when Y content was 1.08 wt.%, the alloy mainly contained I-phase and α -Mg matrix, whereas when Y content was 1.97 or 3.08 wt.%, besides (Mg–Zn–Y phases) I-phase and α -Mg matrix, W-phase would be formed. W-phase closely depended on the Zn/Y ratio of the alloys. Microstructure observation shows that with the addition of element Y, Mg–Zn–Y phases are formed at the grain boundaries. From the previous investigations, the ratio of Zn in the base alloy (2.0-3.0) wt % and the percentage of Y addition were at low ratio, which was selected in this investigation. The aim of this study is to investigate the microstructure, phase constitutions and mechanical properties of as-cast ZRE1 magnesium alloy, with the addition of an individual rare earth metal, 0.75 wt.% Y into the Mg–Zn–RE–Zr alloys.

EXPERIMENT PROCEDURE

ZRE 1 magnesium cast alloy was used as a base alloy. Table-1 shows the chemical composition of the as-cast ZRE1 magnesium alloy.

Table-1. Chemical composition of the ZRE1 alloy (wt. %).

Mg	Zn	*RE	Zr
Balance	2.0-3.0	2.5-4.0	0.4-1.0

*RE- Ce- rich mischmetal.

Melting of the base alloy was conducted in an electrical resistance furnace with a steel crucible under a cover gas mixture of Ar and 2% SF₆. 0.75 wt.% of 99.9% yttrium was added as small pieces, after the base alloy melted around 730 °C and then the temperature was kept at 730 °C with stirring for a few minutes to ensure dissolution of alloying elements. Then, molten metal was poured in a steel mold (preheated up to 500 °C) at 730 °C. The samples taken from the central section of ingots were grinding with silicon carbide papers and a final grinding is done by 1200 /2400 grit papers, followed by polishing with 0.3 micron α -alumina.

The hardness measurements were obtained using Matsuzawa DVK-2Vickers hardness device. Each reading represents an average of seven measurements. The microstructure observations are determined using Nikon optical microscope device, with a maximum objective lens magnification of 1000x, and Scanning Electron Microscopy SEM (JEOL- JSM-6380LA), equipped with an EDS detector. IMT iSolution DT V12.0 image analyser was used to examine the microstructure. X-ray diffraction (XRD, BRUKER-D8 ADVANCE) was utilized for phase

identification; the samples were scanned over a range of 20° to 80° at a step size of 0.020° and 15.4 sec/step.

RESULTS AND DISCUSSIONS

Microstructure

The microstructures of ZRE1 and ZRE1+0.75 Y alloys are shown in Figure-1. It can be seen that the microstructure of the base alloy was changed, with the addition of Y and the grains number increased, which means that the grain size was reduced by Y addition. Generally, rare earth elements have grain refinement effects on magnesium alloys. Using the intercept method specified in ASTM E112-04, the average grain sizes of base alloy and base alloy+0.75 Y can be determined about 72.40 μm and 49.13 μm respectively. Therefore, it can be concluded that Y addition to ZRE1 alloy is effective to refine grains of the alloy. The result of grain size refinement has a good agreement with (Xu, Tang *et al.* 2007), where they reported that the grain sizes of the as-cast Mg–Zn–Zr alloy significantly decreased, with the addition of Y, where the highest reduction of grain was about 65% at 3.08 wt.% Y. In addition, (Xu, Tang *et al.* 2007) reported that the refinement effects of element Y can be mainly ascribed to that of Y can change the solution degree of Zn, which decreased the solidus curve and time for nucleation and then reduced the grain size.

SEM observations showed that the microstructure of base alloy consists of α -Mg grains, surrounded by second phase crystallized along the grain boundaries, as a kind of massive morphology as shown in Figure-2. The EDS results showed that the matrix contains magnesium, zinc and a small amount of zirconium, (Marked 1). In addition, second phase was composed of magnesium, zinc, cerium as shown in Figure-2 (Marked 2). It showed that the base alloy consisted of two phases, the α -Mg matrix and Mg–Zn–Ce intermetallic compound. (Rzychoń, Szala *et al.* 2012), has written molecular formula of the second phase as (Mg, Zn)₁₂Ce. SEM observation and EDS results of ZRE1+0.75Y alloy are shown in Figure-3. It shows that α -Mg matrix phase contains Mg, Zn, Zr, which means that Y combined with the intermetallic phase, thus continuously distributed along the grain boundaries. New second phase formed with the Y addition on Mg–Zn–Y–Ce alloy. Combination of alloying rare earths with elements decreasing the solubility of rare earths in Mg and simultaneously forming thermally stable plate shaped particles on the basal planes. This is clearly a promising method of developing creep resistant magnesium alloys (Friedrich and Mordike 2006).

The XRD patterns of ZRE1 and ZRE1+0.75 Y alloys are shown in Figure-4. It can be observed that there is no other phases were formed. Moreover, the peak intensities of Mg-phase decreased with the Y addition. Otherwise, Mg RE-phase was slightly increased. Therefore, during solidification, rare earth elements formed (Mg, Zn) RE phase, until all the available RE was used, without any formation with other phases.

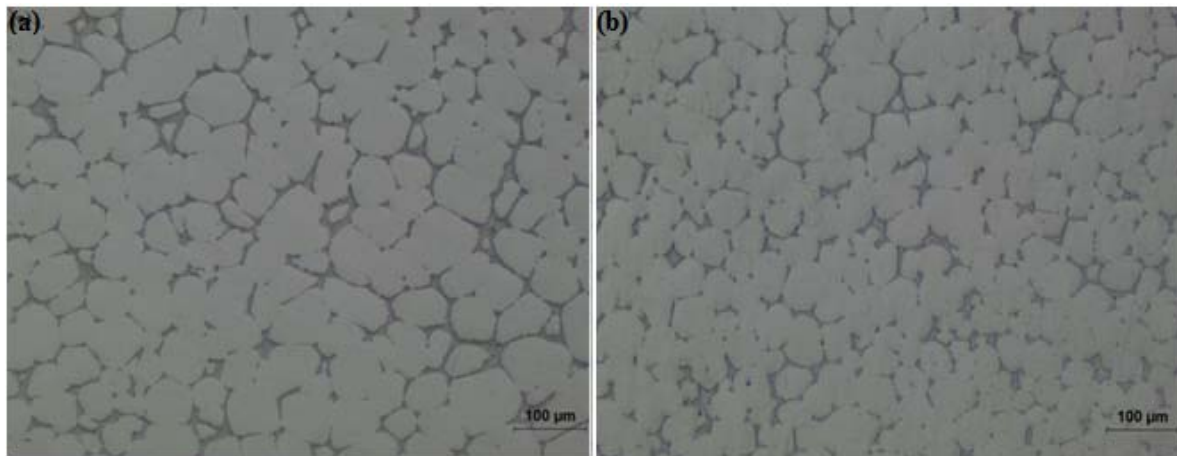


Figure-1. OM microstructures of magnesium alloys: (a) ZRE1 alloy; (b) ZRE1+0.75 Y.

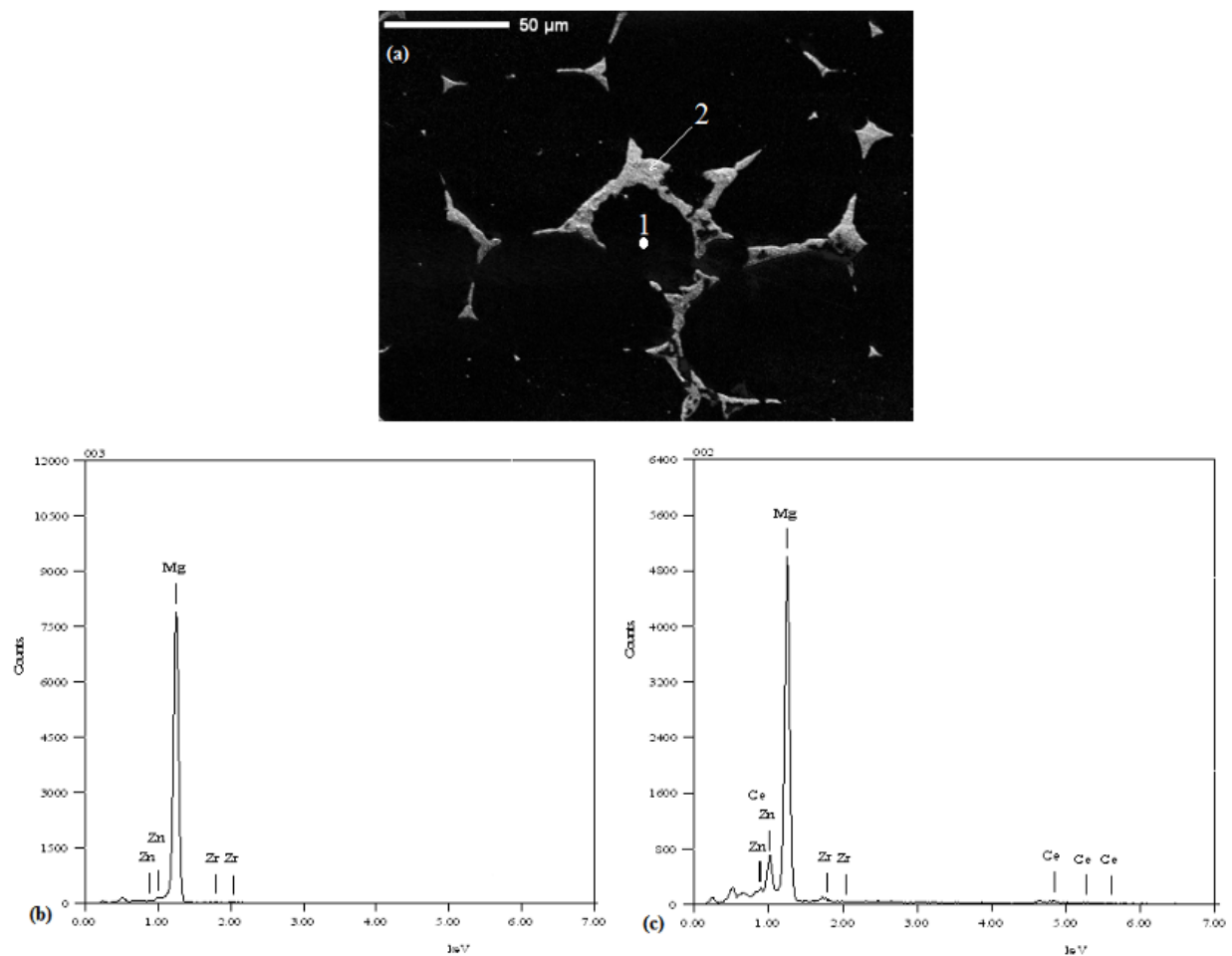


Figure-2. (a) SEM micrograph of ZRE1 magnesium alloy, (b and c) EDS microanalysis of matrix (point 1: Mg-Zn-Zr), and second phase (point 2: Mg-Zn-Ce).

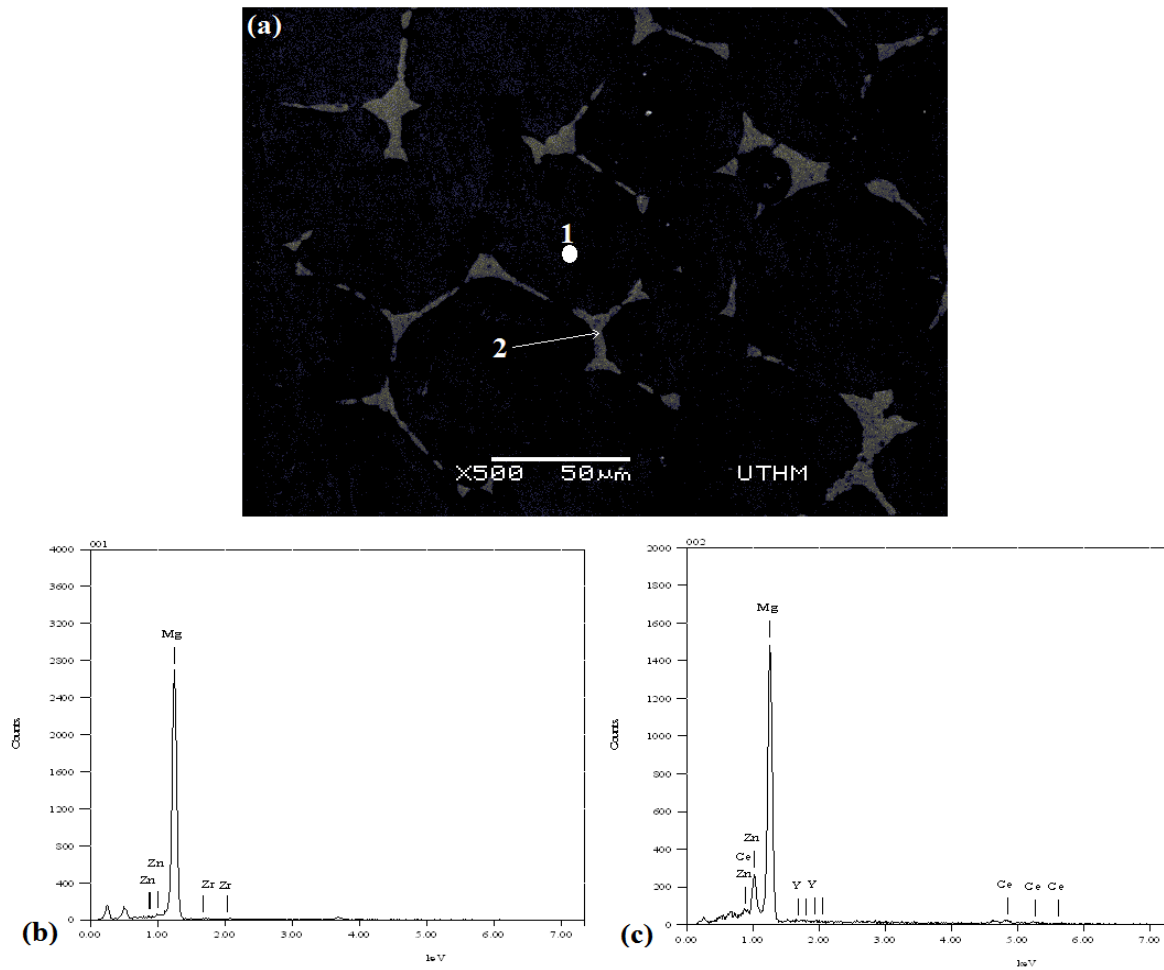


Figure-3. (a) SEM micrograph of ZRE1+0.75 Y alloy, and EDS microanalysis of marked points: (b) point 1 Mg-Zn-Zr and (c) point 2 Mg-Zn-Y-Ce.

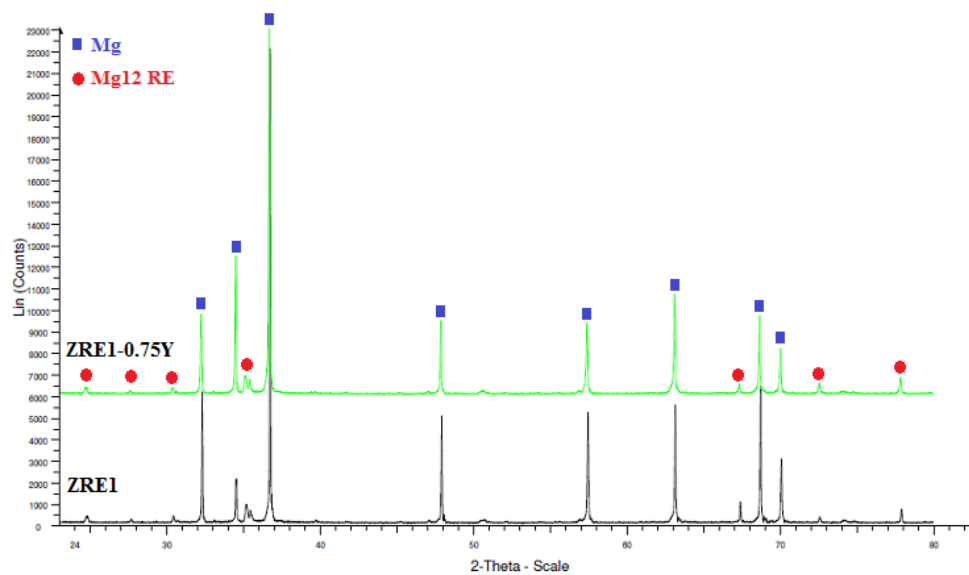


Figure-4. XRD patterns of ZRE1 and ZRE1+0.75 Y alloys.



Hardness test

Figure-5 shows hardness of the base alloy and base alloy+0.75Y. It can be seen that the hardness was improved at 56.6 HV, with the addition of 0.75wt.% Y. The increase in hardness with the Y addition is due to the grain refinement, where the grain size was decreased by 32 % and the hardness improved by 13 %. Moreover, the improvement of hardness is due to the second phase (Mg₁₂Zn)₂ RE, intermetallic compound (Mg-Zn-Y-Ce). (Yang, Li *et al.*, 2008) reported that Mg₁₂RE is a strengthening phase of MEZ (Mg-Zn-RE) alloys. Similar results were obtained by (Boby, Ravikumar *et al.*, 2013). They reported that hardness of AZ91 increased with 0.9 wt.% Y addition. However, it is known that the mechanical properties of magnesium alloys are improved by rare earth additions (Rokhlin 1998). Similar results were obtained by the Pr addition, with the hardness of AZ61 improved with 2 wt.% Pr (Zhiyong, Jingjing *et al.*, 2014).

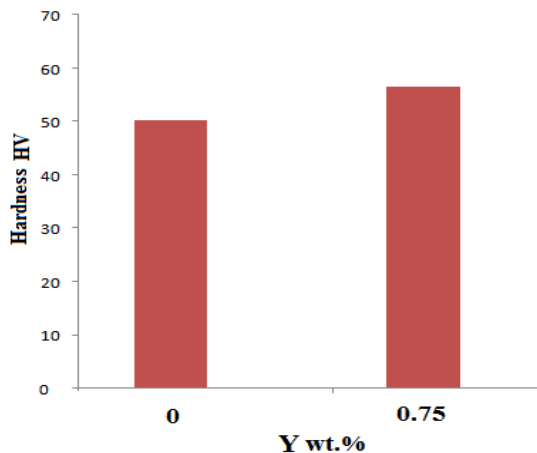


Figure-5. The hardness values of as-cast base alloy and base alloy+0.75Y.

CONCLUSIONS

The effect of the addition of Y on the microstructure and hardness of ZRE1 cast alloy was investigated. Thus, the following can be summarized:

- The Y addition has significant effect on grain size, while the grain refinement and size reduced by 32%.
- New intermetallic phase was formed by the Y addition with alloy elements (Mg-Zn-Y-Ce), which distributed along the grain boundaries.
- The hardness of ZRE1 was improved by 13% with the Y addition.

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REFERENCES

Boby, Arun, Ravikumar, Kk., Pillai, Uts and Pai, Bc. 2013. Effect of Antimony and Yttrium addition on the

high temperature properties of AZ91 Magnesium Alloy. *Procedia Engineering*, 55, pp. 98-102.

Castor, Stephen B and Hedrick, James B. 2006. Rare earth elements. *Industrial minerals volume*, 7th edition: Society for mining, metallurgy, and exploration, Littleton, Colorado, pp.769-792.

Davis, Joseph R. 2001. *Alloying: understanding the basics*, ASM international.

Davis, Joseph R. 2009. *ASM handbook. 2. Properties and selection: nonferrous alloys and special-purpose materials*, ASM international.

Dobrzański, La., Król, M and Tański, T. 2010. Effect of cooling rate and aluminum contents on the Mg-Al-Zn alloys' structure and mechanical properties. *Journal of Achievements in Materials and Manufacturing Engineering*, 43(2), pp.613-633.

Ferro, R., Saccone, A and Delfino, S. 2013. Magnesium alloys of the rare earth metals: systematics and properties. *Metallurgical Science and Technology*, 16(1).

Friedrich, Horst E and Mordike, Barry L. 2006. *Magnesium Casting Alloys*. *Magnesium Technology: Metallurgy, Design Data, Applications*, pp.145-218.

Rokhlin, Li. 1998. *Advanced Magnesium Alloys with Rare-Earth Metal Additions*. *Advanced Light Alloys and Composites*, Springer, 443-448.

Rzychoń, Tomasz, Szala, Janusz and Kielbus, Andrzej. 2012. Microstructure, castability, microstructural stability and mechanical properties of ZRE1 magnesium alloy. *Archives of Metallurgy and Materials*, 57(1), pp. 245-252.

Xu, Dk., Tang, Wn., Liu, Lu., Xu, Yb and Han, Eh. 2007. Effect of Y concentration on the microstructure and mechanical properties of as-cast Mg-Zn-Y-Zr alloys. *Journal of Alloys and Compounds*, 432(1), pp. 129-134.

Yang, Zhong, Li, Jp, Zhang, Jx, Lorimer, Gw and Robson, Jamsel. 2008. Review on research and development of magnesium alloys. *Acta Metallurgica Sinica (English Letters)*, 21(5), pp.313-328.

Zhiyong, You., Jingjing, Kang., Wenbo, Zhang and Jinshan, Zhang. 2014. Effect of Pr addition on microstructure and mechanical properties of AZ61 magnesium alloy. *Research and Development*, 11(2).