Visual Abstract

Age-hardening heat treatment behavior of as-cast Mg–Zn–Al alloys

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ABSTRACT. Magnesium alloys have generated renewed interest as a light alloys; replacing some conventional structural materials for weight reduction in applications like aerospace, automotive and electronics industries. In interior components and powertrains, cast alloys are widely used and represent more than 99% of magnesium alloys used today, whereas only a few wrought products are used. Mostly in automotive applications, Mg-engine block can noticeably reduce the weight and consequently its fuel consumption and environmental impact. Due to solid-state precipitates, these alloys are strong in nature and are produced by an age-hardening heat treatment process. In the present work the age-hardening behavior of the as cast Mg–Zn–Al alloys (ZA85 alloy) in the composition of 8 wt. %Zn, 5 wt. %Al has been investigated. Through the differential thermal analysis (DTA) studies, it has been found out that dissolution temperature of ternary eutectic precipitates is present in the alloy. Based on the DTA results, the as cast samples have been solutionised at 360 °C temperature for different intervals of time. Solutionising time has been optimized from the enthalpy values of un-dissolved precipitates. The solution treated samples have been then aged at temperature of 180° C for different time intervals. From the peak hardness values, the ageing conditions have been optimized.

KEYWORDS. Magnesium alloy ZA85; DTA; Solution treatment; Ageing; Microstructure; Hardness.

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INTRODUCTION

Magnesium alloys is a promising material for the fabrication of automotive, aerospace and electronics components. So far, most Mg alloys have been used in automotive components like the steering wheels, disk wheels, gear box, chain locker instrument panels, and seat frames and crank cases where, the operating temperature is low, due to its light weight could help car manufacturers to reduce the amount of emissions generated per automobile and to meet present and future regulations looking for more environmentally friendly vehicles [1, 2]. For instance, its usage for automotive parts requiring low mass and low specific weight has been found to reduce fuel consumption by 20-25% [2]. However, the low strength of magnesium alloys compared to aluminium and steel have limited its use in many areas. In order to improve the hardness of magnesium alloys, solid solution, grain size and dislocation density strengthening which either depends on the composition and thermal treatment processes had been widely studied, but precipitation strengthening mechanism has the highest strengthening effect. The precipitation hardening involves the addition of alloying elements along with heat treatments in order to synergistically bring about the strengthening required for the Mg alloy. These had been the focus of numerous investigations in recent times. Among the Mg-based alloys, Magnesium-zinc (Mg-Zn) alloys shows the highest precipitation hardening response; therefore, it has been found that the properties of this alloy improved significantly when combined with calcium (Ca) [1]. The Mg-Zn alloys with addition of Ca has been reported to increase the effectiveness of precipitation hardening when the alloy is exposed to ageing, causing a higher quantity of finer and uniformly dispersed precipitates, that influences the final texture of the alloy significantly [2-5] and Ca addition also decreases the grain size in microstructure that leads to improvement in mechanical properties of the alloy [6], moreover it decreases the flammability of the alloy and increases creep and oxidation resistance [7-11]. It is difficulty to process Mg-alloys; different deformation mechanism present and anisotropy when loaded under tension/compression are major challenges, which limit their application in automotive industries [12-15]. That can be overcome by using Mg-alloys with rare earth (RE) elements such as Ce, Gd, Nd and Y developed for high temperature applications in the aerospace industries but these alloys are very expensive[16]. Hence, the development of heat resistant Mg-alloy at low cost is the major challenge in automotive sector. Recent studies [17-18] have reported that the Mg-Zn-Al system having Zn-Al composition in the ratio of 2:1 has sound creep resistance. It is also reported that ZA85 alloy is one such alloy system having superior elevated temperature behaviour and satisfies the requirement of other corrosion and foundry properties [19]. The mechanical properties such as strength, ductility and fracture toughness of this alloy can be further improved by adopting suitable heat treatment procedure. However, each heat treatment procedure such as solutionising temperature, time and the ageing conditions significantly influence properties and microstructural changes [20]. Differential Thermal Analyser (DTA) is a powerful tool which is normally used to measure the rate of phase transformation in the alloys such as, precipitation of additional volume fraction of precipitates through fresh nucleation or growth of existing precipitates, progressive dissolution of precipitates, on-going coarsening of precipitates and precipitation of new phases [21-22]. The present work investigated the age-hardening behaviour of the as cast Mg–Zn–Al alloys (ZA85 alloy) using DTA studies and other conventional methods.

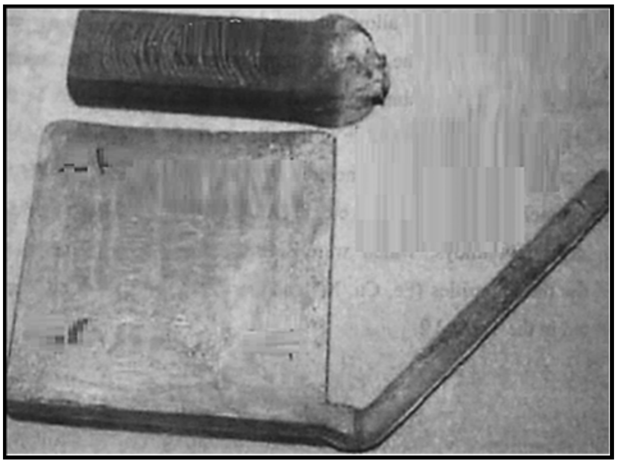


Figure 1: Image of Mg-alloy casting

MATERIALS AND EXPERIMENTAL METHODS

Alloy Preparation and Casting Procedures

In experiments, permanent cast iron mold castings method was used and initially, no pouring basin attachment with the sprue was there, which led to a restriction in pouring speed as higher pouring speed led to the spilling of molten metal into the floor. Before the casting, the properly cleaned mold was given a graphite coat and preheated to 310°C in a heating oven for 60-70 minutes. Resistance box furnace was used for melting of magnesium alloys. The preheated

flux was sprinkled in the bottom and side of the cleaned crucible and kept inside the furnace. After the complete melting of the metals in the crucible, the refining of melt was carried out at a temperature of 700°C. After the refining and settling process was over, the molten metal was poured into the pre heated molds. Pouring was carried out smoothly without any jerk in the melt, as excessive jerk disturbs the settled oxide inclusions in the bottom. The flux layer near the lip of the crucible was pulled back softly by using a skimmer for smooth flow of molten metal. The oxygen around the melt jet was removed by sulfur dusting. Three fourth of the melt in the crucible was poured into the preheated mould. The remaining metal was poured separately as a scrap. Fig. 1 shows an image of one such Mg-alloy casting samples.
The chemical compositions of Mg-alloy ZA85 are presented in Tab. 1.

Zn	Al	Mn	Mg
8	5	0.2	Balanced

Table 1: Chemical compositions of Mg-alloy ZA85 (wt. %).

Thermal Analysis
The differential thermal analysis (DTA) measurements were carried out on as cast samples of ZA85 alloy to find out the dissolution temperature of eutectic ternary phase using differential thermal analyzer under argon atmosphere with a heating rate 10 °C min^{-1}. From the DTA results, solutionising temperature was identified as 360 °C. Then, the samples were solution treated using the heat treatment schedule presented in Tab. 2. The DTA measurements were performed on all the samples immediately after solution treatment to find out the time required for maximum dissolution of the precipitates into the matrix. At least three runs were carried out to confirm the results.

Heat Treatment
The samples (cylindrical pieces of 20mm×15mm) were machined out from the castings of ZA85. These samples were heat treated in a muffle furnace under carbon dioxide atmosphere for different schedules given in Tab. 2.

Alloy Code	Heat Treatment Parameters
Z_1	As cast
Z_2	Solution treated at 360°C for 24 hours, quenched in water at 32°C
Z_3	Solution treated at 360°C for 48 hours, quenched in water at 32°C
Z_4	Solution treated at 360°C for 72 hours, quenched in water at 32 C
Z_5	Solution treated at 360°C for 96 hours, quenched in water at 32°C

Table 2: Heat treatment schedule for Mg-alloy ZA85.

The samples were solution treated for optimum condition and they were aged at 180°C for 36 hours. Every 2 hours, samples were drawn from the furnace and the hardness measurements were carried out.

Hardness Testing
SIGMA hardness machine was used for Brinell hardness measurement of as cast and heat-treated samples. For hardness measurement one side of the specimen was polished with 600 grit size emery paper to remove the oxide and other scales in order to see the edges of the indentation mark clearly. A 3 mm ball was used to make indentation. Load was fixed at 100 kg with a dwell time of 30 sec. On an average five indentations were made and average value is recorded.

Microstructure
Both the cast and heat-treated samples were initially paper polished with different grit size 100, 220, 400 and 600 μm Silicon Carbide emery papers, subsequently they were polished with 0.25 micrometres diamond paste then they were etched with solution containing 5 g of picric acid, 5 ml acetic acid, 100 ml ethanol and 10 ml distilled water. The 2~3s

etched samples were viewed under microscope with image analysis software. SEM was used to analyse the microstructure of Mg, Zn and Al ternary intermetallic.

X-Ray Diffraction (XRD)

XRD was applied to analyse the phases present in heat treated samples using PANalytical X-ray diffractometer. X-rays are electromagnetic waves with short wavelength. The interaction of the X-ray beam and the electrons in atoms causes diffraction. The energy dispersive spectroscope (EDS) studies were also carried out using Jeol SEM to analyse the compositions of Mg, Zn and Al bearing intermetallic.

RESULTS AND DISCUSSION

Microstructure Analysis

The optical micrographs of permanent mould as cast ZA85 alloy is represented in Fig. 2(a). From this, it is observed that, the microstructure of Mg-alloy ZA85 contains α(HCP) Mg-matrix, coarse ternary intermetallic phases and γ (Mg_4-Zn_{11}-Al) stable phase at the grain boundaries. In ZA85 alloy, the solidification starts with crystallization of α-Mg in the dendrite region and forms $Mg_{17}Al_{12}$ eutectic compound at moderate temperature. On further cooling, the metastable Mg_{17}-Al_{12} phase reacts with Zn in the liquid and forms many possible Mg-Zn-Al ternary intermetallic compounds [18]. Similar investigations on ZA84 (Mg-8Zn-4Al) alloy confirm that the ternary intermetallic found in this alloy is a metastable icosahedra quasi-crystal of point group M35 with a small fraction of equilibrium γ-phase [19]. In the present work, X-ray diffraction of quasi-crystal ternary intermetallic could not be identified because of the imperfect match of its standard spectrum in the diffraction data software. However, the EDS result as shown in Fig. 2(b) confirms the presence of coarse intermetallic phase of Mg/Zn/Al having ratio 66/16/17. It is further noticed that this ternary intermetallic phase ratio varies with different locations in the microstructure of Mg_x-Zn_y-Al_z type.

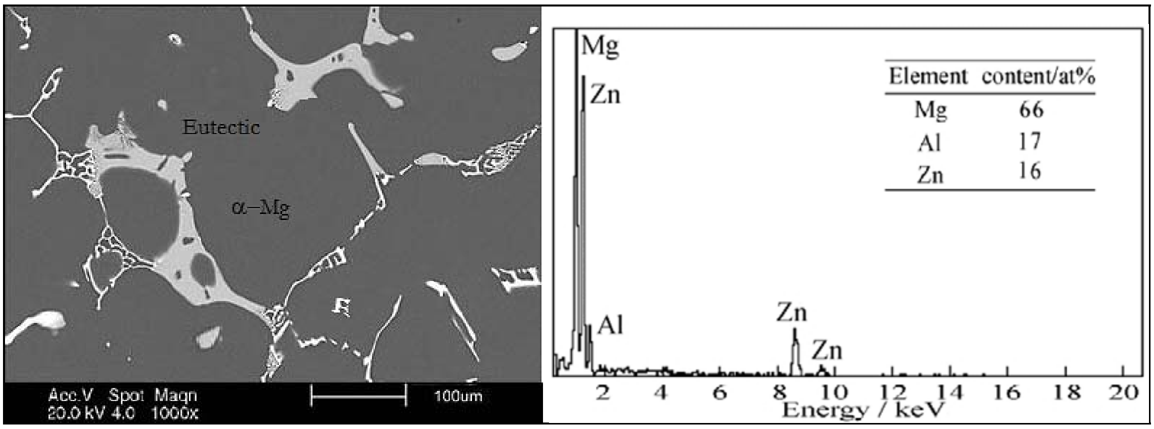


Figure 2: (a) SEM micrograph of as cast Mg-alloy (b) SEM-EDS of eutectic ternary phase

Effect of Solution Treatment

The differential thermal analysis (DTA) thermograph of ZA85 alloy is shown in Fig. 3. It is observed from this figure that the endothermic peak at 361.08°C for the as cast sample corresponding to the ternary eutectic dissolution temperature. It is difficult to identify the other peaks of many possible Mg_x-Zn_y-Al_z phases present in the alloy mainly because oxidation of this alloy starts above 450°C. It can be further observed from the DTA results that liquidus temperature of ZA85 alloy is 597.17 °C which is equivalent to liquidus temperature of commercial AZ91 alloy (598 °C), entailing good castability of alloy. From the DTA investigation, the solutionising temperature of the alloy is determined as 360 °C, which is slightly lower than the dissolution temperature.

During solution treatment, the intermetallics present in the alloy get dissolved into the α-Mg matrix and form a supersaturated solution while quenching. However, the homogenization and micro-segregation depend upon the solutionising temperature, time and the solubility range. Fig. 4 shows the X-Ray Diffraction (XRD) analysis for the as cast and ST samples at 360°C for different intervals of times. It is observed from the Fig. 4 that complete dissolution of $Mg_4Zn_{11}Al$ has taken place after 24 hours of holding.

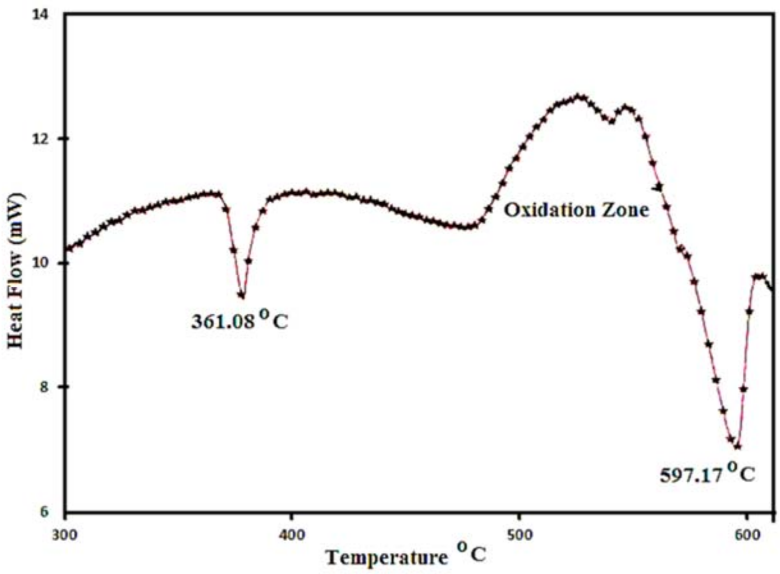


Figure 3: DTA thermograph (Heating rate of 10 °C min^{-1})

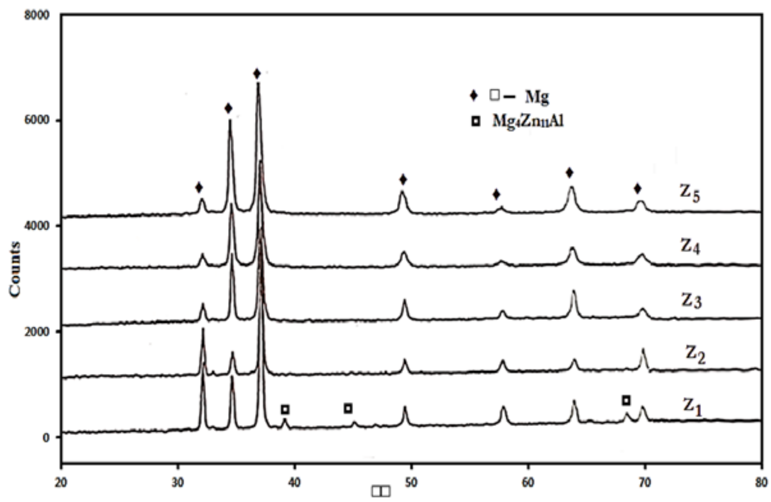
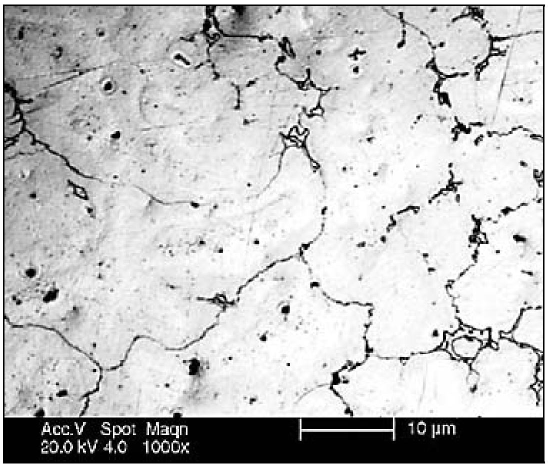


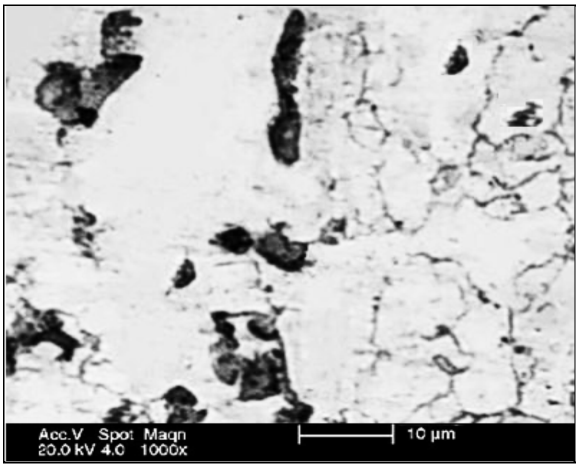
Figure 4: X-ray diffraction pattern of as cast and Solution treated samples

Fig. 5 presents the micrographs of ZA85 alloy with respect to different solutionizing times. It is noticed from this figure, that there is significant change in the microstructure with increase in solutionising time. Even though, the microstructure of Z_2 condition reveals the complete dissolution of γ-phase to supersaturated solid solution, however the presence of Mg-matrix with some eutectic ternary phases can be seen. The microstructures of Z_3 and Z_5 conditioned alloys presented in figures 5b-c show the presence of considerable volume fraction of precipitates, which are distributed along the grain boundaries even after increasing the solutionising time. Further, DTA analyses have been carried out to find out the time required for dissolution of maximum number of precipitates.

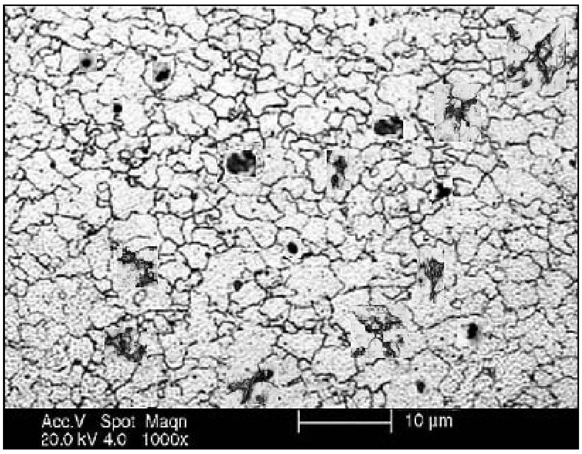
The DTA studies carried out on the as cast and the solution treated samples at 360 °C for varying time intervals (24, 48, 72 and 96 hrs) are exhibited in Fig. 6. The peak temperature for eutectic dissolution and the enthalpy calculated from the DTA thermographs for all the samples are given in Tab. 3. It is observed from the DTA results that the enthalpy decreases with increase in solutionising time due to dissolution of precipitates into the matrix. The reduction in enthalpy from 0 to 24 hrs is marginal because of the insufficient time given for dissolution of precipitates into the matrix but the reduction in enthalpy is drastic from 24-48hrs. For prolonged time (up to 96 hrs) of solution treatment, considerable amount of endothermic reaction observed in the in DTA studies confirm the presence of precipitates but in a lower volume observed in the microstructure. This can be further explained that the maximum solid solubility of (6.22 wt %) Zn atoms contributing to the dissolution of precipitates into matrix; the residual Zn atoms (beyond 6.22 wt %) does not respond to the solution treatment temperature and time.



(a) As cast



(b) Solution treated at 360 °C for 48 hours



(c) Solution treated at 360 °C for 96 hours

Figure 5: Micrographs of Mg-alloy ZA85.

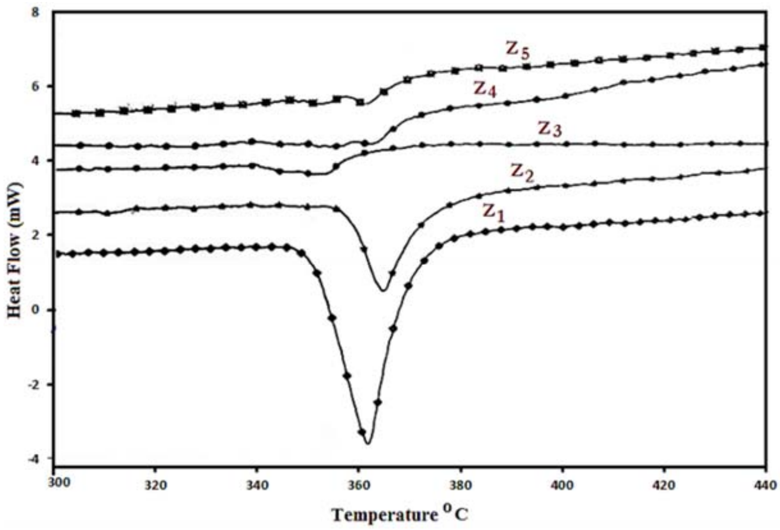


Figure 6: DTA curve of as cast and solutionised samples at different time intervals.

Alloy Code	Peak temperature in 1 °C	Enthalpy (J/g)
Z_1	361.08	63.9112
Z_2	362.87	44.9931
Z_3	353.06	18.0056
Z_4	360.05	15.9620
Z_5	359.89	14.9629

Table 3: Peak temperature (±1 °C) and enthalpy values for endothermic reaction in the as cast and solutionised samples

The Brinell hardness values of the solution treated samples also show similar trend as shown in Fig. 7. It is evident from the hardness results that the minimum time required for dissolution of maximum ternary eutectic phase in the solution treated conditions is 48 hours at 360 °C.

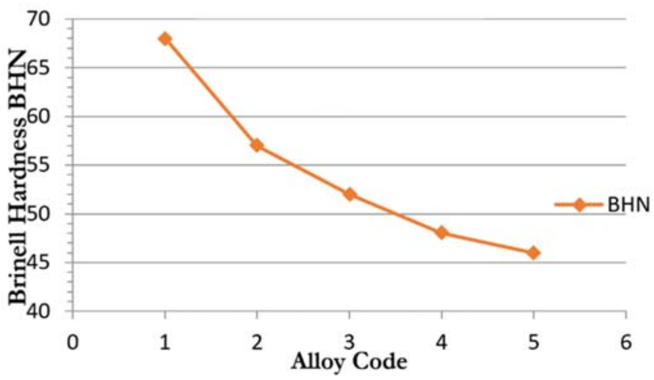


Figure 7: Brinell hardness for as Cast and ST samples

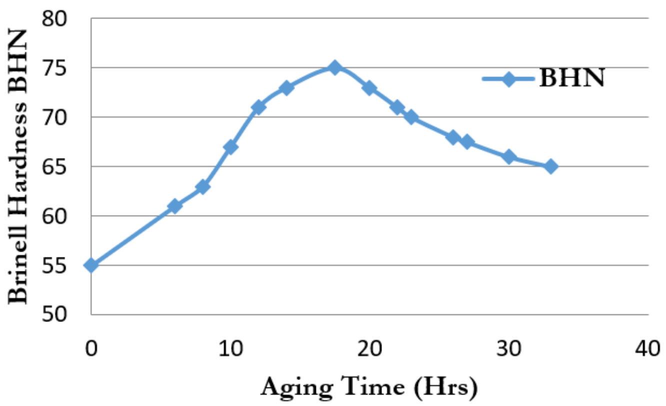


Figure 8: Hardness variation with different aging time

Effect of Age-Hardening

The hardness values as a function of ageing time at 180 °C are shown in Fig. 8. It is observed from this figure that the hardness increases with increasing ageing time and the maximum hardness is obtained at 17 hours of aging; beyond that it decreases. This maximum hardness attained is associated with the optimum temperature and time. While increasing ageing time, the particles become coarser and they are less effective in retarding the dislocation motion during deformation. The formation of particles to an optimum size and uniform inter particle spacing thereby increase the strain field of phase/matrix interface. The microstructure of optimum aged (180 °C for 17 hours) ZA85 alloy displayed in Fig. 9 shows the presence of fine eutectic ternary phases distributed uniformly along the grain boundaries, which act as an effective straddle to dislocation motion thereby improving the properties of ZA85 alloy.

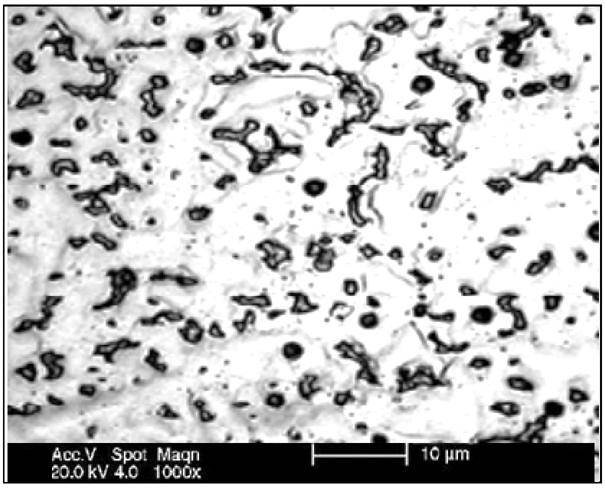


Figure 9: Micrographs of optimum aged sample.

Conclusions

In this research work, experimentation was conducted to investigate age-hardening heat treatment behaviour of the as-cast Mg-alloy-ZA85. Based on the experimental results, the conclusions drawn are:

a. The liquidus temperature of Mg alloy ZA85 is 597.17°C, whereas the dissolution temperature of ternary eutectic precipitate is 360 °C

b. To achieve the maximum strength properties in Mg alloy ZA85, the following heat treatment process needs to be followed:

Solution Treatment: 360 °C ± 5 °C for 48 hours

Water quenching at 32 °C

Age-hardening: 180 °C ± 2 °C for 17 hours

c. The hardness values increases with increasing ageing time and the maximum hardness is attained at 17 hours of aging beyond that hardness values decreases. This maximum hardness attained is associated with the optimum temperature and time.

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