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EFFECT OF PAINT-BAKE LIKE TREATMENT ON MECHANICAL PROPERTIES OF Mg-Zn-Ca ALLOY

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ABSTRACT
Magnesium alloys are promising materials for the fabrication of automotive components due to their lightweight which could help car manufacturers reduce the amount of emissions generated per automobile and to meet present and future regulations of owning more environmentally friendly vehicles. However, the low strength of magnesium alloys compared to aluminium and steel have limited its usage and has necessitated the search for more potent strengthening mechanism, like precipitation strengthening, to widen the application of magnesium alloys in the automotive industries. Precipitation hardening response of a Mg-4wt%Zn-0.3wt%Ca (ZX40) alloy in an ageing process at 180°C temperature typical of those used during paint baking cycle in automotive industries were studied using optical microscopy, Scanning electron microscopy (SEM), micro-hardness and thermoelectric power machine (TEP). Prior to the ageing process, one alloy was subjected to a 30minutes solution heat treatment while the other sample was without solution heat treatment. Although, an initial decrease in hardness and strength of the alloy was observed due to solution treatment prior to ageing. The overall results showed that the mechanical (strength and hardness) and microstructure (fracture surface and precipitate formation) properties were enhanced in the 30minutes solution treated samples, which further emphasizes the need for solution treatment for better properties in an alloy.

Keywords: *Paint baking, Magnesium alloys, Precipitation strengthening, scanning electron microscopy*

1. INTRODUCTION
Magnesium alloy, a promising material for the fabrication of automotive components like the disk wheels, gear box, chain locker and crank cases to mention a few, due to its light weight could help car manufacturers 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 high specific weight has been found to reduce fuel consumption by 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. Magnesium-zinc (Mg-Zn) alloys exhibit the highest precipitation hardening response amongst Mg-based alloys, thus the properties of this alloy has been found to improve significantly when combined with alloying additions of calcium (Ca) [1]. The addition of Ca to Mg-Zn alloys has been reported to increase the potency of precipitation hardening when the alloy is exposed to ageing, producing a higher amount of finer and uniformly dispersed precipitates, which influences the final texture of the alloy significantly [2-5]. Ca additions also reduce the grain size in the microstructure leading to improvement the mechanical properties of the alloy [6], but decreases the flammability of the alloy and increases creep and

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oxidation resistance [7-11]. The difficulty of processing Mg alloys, different deformation mechanism present and anisotropy when loaded under tension and compression are major challenges limiting its use in the automotive industries [12-15]. Researchers are continually studying ways to reduce the cost of processing magnesium alloys as well as overcoming the aforementioned challenges [15]. Paint baking process that doubles as an anti-corrosion coating and ageing process has been studied in aluminium alloys and the results have been encouraging so far, especially at a controlled temperature and time [16-20]. The paint baking process on AZ31 and AZ80 Mg alloys as conducted by Sha Ming-hong*et al.* [21] showed no significant changes in the hardness due to the slow ageing kinetics of the alloy. The response of the Mg-4wt%Zn-0.3wt%Ca alloy (ZX40) to heat treatments typical of those used in the automotive industry, specifically the suitability of ageing the alloy during the paint bake processing cycle used in automotive industries will be studied in this project.

2. MATERIALS AND METHODS

Ingots of ZX40 Mg alloys with starting dimensions of 150x45x10mm were reduced in a Struersaccutom machine to 5x8x5mm in a multiple operations of hot-rolling, solution treatment and water quenching.

Since the automotive industries would not likely subject the alloy to solution treatment prior to the paint-baking processes. Prior to the paint baking cycles, the ageing process was carried without previous solution treatment and with solution treatment at 400°C for 30 minutes. The two sample set were then subjected to ageing temperatures of 180°C in a Lenton furnace type 3216 under an argon atmosphere for 1hour typical of those of a typical paint baking cycle. The alloy was further exposed to longer ageing times of 3, 5, 8, 24 and 48hours in order to assess the behaviour of the alloy.

After the ageing treatment, the samples were mounted in a hot compression thermosetting resin at 150°C with a heating time of 7 minutes. This was followed by grinding in four (4) consecutive steps, with a 200, 400, 800 & 1200 grain size sand paper using water as a lubricant. After grinding, samples were polished in a Buehler Metaserv Universal Polisher machine with different size diamond particle abrasives; 6, 1, and ¼ of a micron particle size, ethanol was used to wash samples between the polishing steps to avoid oxidation in the surface.

StruersDuraminVicker hardness tester, with a 0.2kg load and dwell time of 10s was used to take the hardness values to estimate the strengthening achieved by precipitation hardening. To view the morphology of the samples before and after ageing, an Olympus BH2-UMA microscope was used to view the Mg-Zn-Ca alloy surface. A more detailed microstructure examination was carried out using a Quanta FEG 650 scanning electron microscope. Thermoelectric power (TEP) measurements were performed in a TechLab TEP machine to assess the relative electrical conductivity of the effect of pre-ageing and solution treatment on samples with different conditions.

3. RESULTS

3.1 Hardness Evolution

Fig. 1 shows the hardness values of the samples which were aged at a temperature typical of a paint baking cycle in the automotive industries without any prior solution heat treatment. Hardness reduction is observed as the ageing time increases, although a slight tendency for increase could be observed after 3hours of ageing, but appears somewhat stable after 48hours.

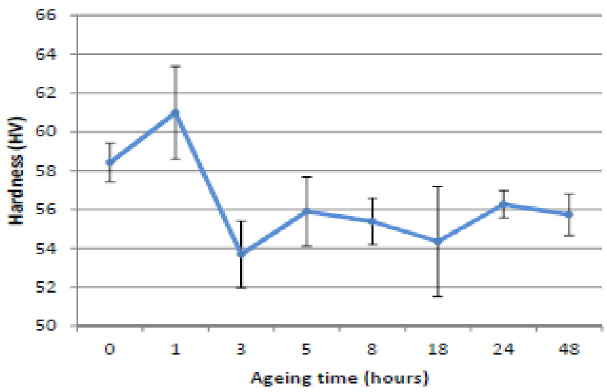

Fig.1: Age Hardening of Mg-Zn-Ca alloys at 180°C without solution treatment

Fig. 2 shows the comparison between the hardness value of the samples aged with and without solution heat treatment. A marked difference exists between the two samples. The hardness values, although decreased at initial time in the solution treated samples, there was a higher tendency to increase at longer ageing times across the profile when compared to the non-solution treated sample.

Optical microscopy images were taken at different ageing times and average grain size measurements were calculated as shown in Fig. 3. A far higher average grain size range of 486μm-586μm for the non solution treated samples is measured compared to 83μm-96μm average grain size range for the solution treated samples at the same ageing times.

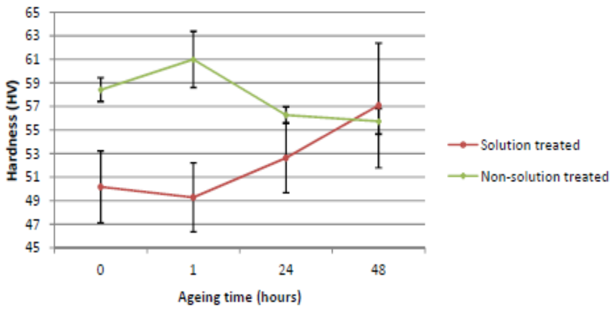

Fig. 2: Comparison of the hardness values of Mg-Zn-Ca alloy samples aged with and without solution heat treatment at 180°C

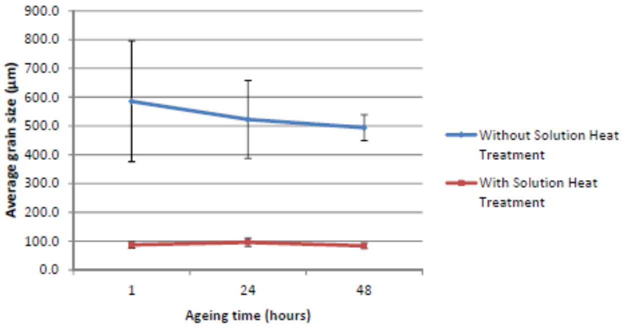

Fig. 3: Average grain size measurements for aged Mg-Zn-Ca samples with and without solution heat treat treatment

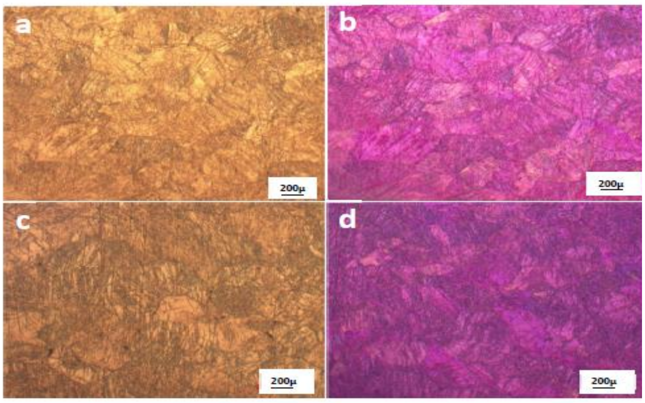

Fig. 4: Optical micrographs of the non-solution treated samples aged for (a-b) 1hour (c-d) 48 hours, Images (b, d) are polarized images.

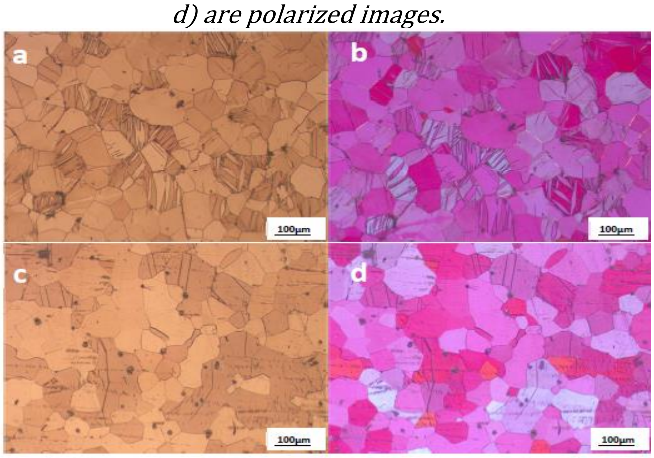

Fig. 5: Optical micrographs of the solution treated aged samples (a-b) 1 hour, (c-d) 48 hours, images (b, d) are polarized images.

3.2Microstructure Properties

A careful observation of Fig. 4 shows no significant difference in the microstructure of the non-solution treated samples. However, a strong texture, high amount of dislocations and twinning is seen from the polarized microscopy images. There is also no evidence of recrystallization and grain size change as observed in Fig. 3 at these low temperatures.

On comparing Fig. 5 to Fig. 4, there were several differences in the micrographs pictured. A clearer recrystallized structure, a much smaller grain size, and a weaker texture from the polarized images identified by the different grain colouration depicted in Fig. 5. Twin boundaries were also observed, though this should have been eliminated by the heat treatments. Large precipitates and impurities are also pictured in Fig. 5(a-d).

3.3 SEM Microscopy

In order to assess the microstructure of the samples at different ageing conditions with and without solution treatment, SEM micrographs were taken in two different magnifications as depicted in Fig. 6 and Fig. 7.

Fig. 6 (a-c) depicts SEM images taken at 50x magnification while (d-f) were taken at 800x magnification. In general, the precipitates that formed within the grain and at grain boundaries at different ageing times vary with size in Figs.6 (a-f). Fig 7(a-b) showed precipitation events occurring at both grain boundaries and within the grains. In addition, there are no substantial differences between the precipitates that formed in these regions. Fig 7(c-d) showed smaller precipitates in the metal matrix.

Comparing Fig. 6 and 7, there was a lower volume fraction of the smaller precipitates in Fig. 7(c and d) than that seen in Fig. 6(d-f).

3.4 TEP Measurements

Fig. 8 shows the relative TEP measurements of the aged samples with and without solution treatment in order to track the precipitation behaviour of the Mg-Zn-Ca under different ageing conditions. Although, a similar trend of increasing conductivity were observed in both alloys, a higher response in the conductivity of the non-solution treated compared to the solution treated alloys could be seen between 1-24 hours of ageing. However, a rather constant trend was observed between 24-48 hours of ageing the non-solution treated alloy as against the reduction trend in the solution treated counterpart, albeit at a slower rate compared to the values between 1-24hours of ageing.

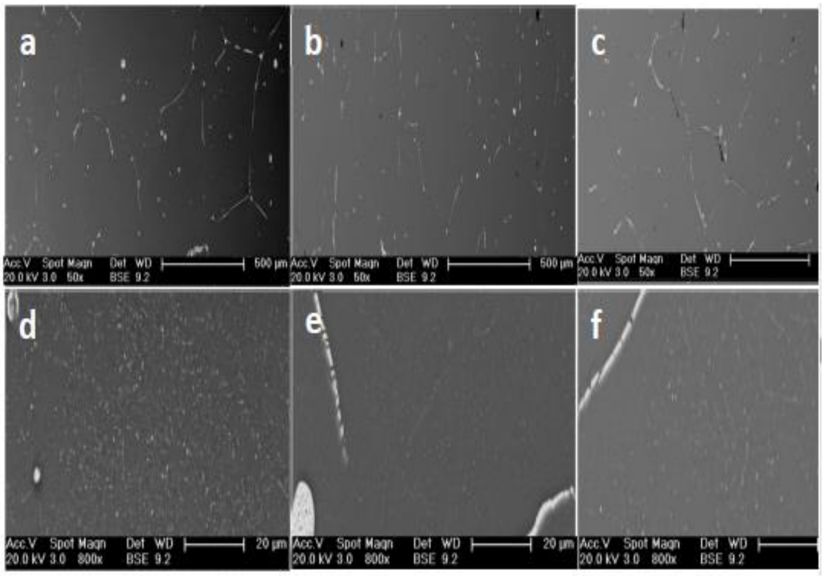

Fig. 6: SEM micrographs of non-solution treated samples at (a, d) without ageing (b, e) 24hours (c, f) 48 hours ageing times.

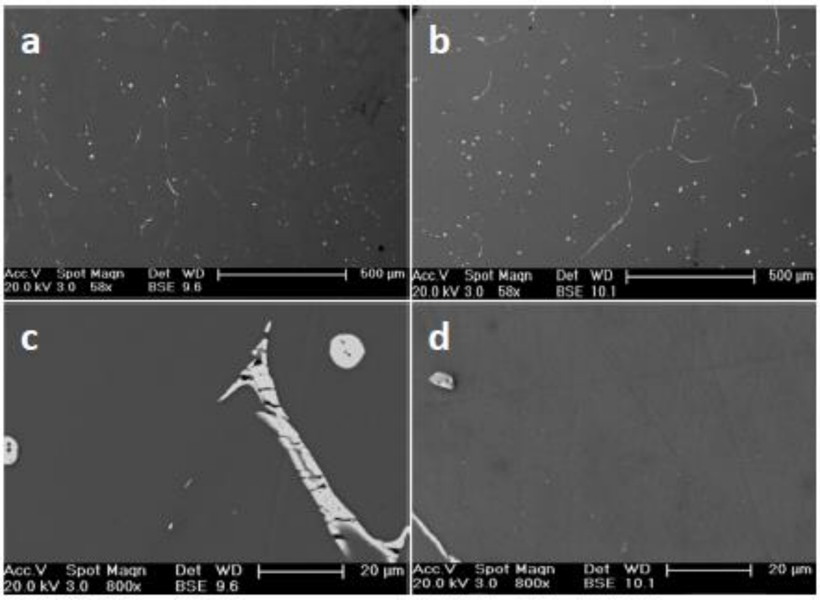

Fig. 7: SEM micrographs of the solution treated samples at ageing times (a-b) 1hour (c-d) 48 hours.

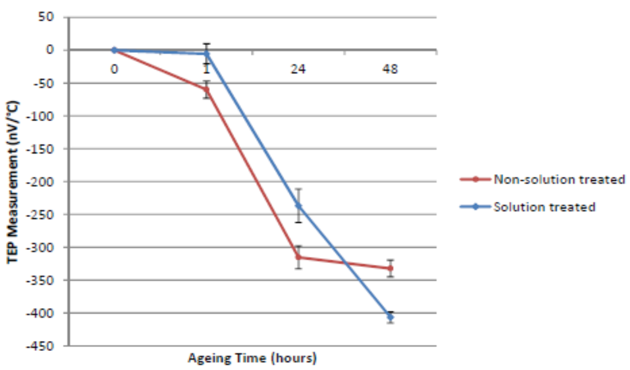

Fig. 8: Relative TEP measurements of solution treated and non-solution treated samples at different ageing times

4. DISCUSSION

The decreased hardness observed in Fig. 1 between 1-24hours of ageing could be attributed to the annealing effect of the ageing temperature, which was responsible for reducing the work hardening rate of the alloy sample. The slight tendency to increase hardness as observed was due to the formation of some precipitates, while the somewhat stable condition seen between 24-48hours indicated that there were no solutes in solution to keep forming the precipitates. This result was confirmed by the slight change in electrical conductivity values between 24-48hours of ageing (-17nV/°C) when TEP measurements were compared to the substantial change (-255nV/°C) observed between 1-24hours.

Comparing the solution treated with the non-solution treated samples in Fig. 2, showed an initial decrease in hardness due to annealing, followed by an uninterrupted increase in hardness up until 48hours and could peak-age after 168 hours according to the study carried out by Bettles*et al* [2] and Langelier*et al* [22]. This result supports the claim of Langelier and his colleagues of the need for longer solution heat treatment so as to increase the amount of solutes in solution needed to enhance the volume fraction of precipitates, thereby contributing to the overall strength of the alloy.

The optical micrographs for the non-solution treated samples (Fig. 4) showed the effect of rolling on the texture of the magnesium alloy, the deformation caused a number of shear bands and twins to appear in the microstructure. The polarized image (Fig. 4 b, d) for all ageing times showed no noticeable difference in grain size or orientation because no recrystallization occurred during this process. On comparing the average grain size of the solution treated with the non-solution treated sample, the decrease in grain size (from 534μm to 89μm) is an evidence of the recrystallization process that occurred during solution heat treatment at 400°C. The weakened texture of the solution treated samples have been attributed to different mechanisms in literature: Particle stimulated nucleation (PSN), shear band induced nucleation (SBIN) and deformation twin induced nucleation (DTIN) [14, 19, 23]. Images b & d from Fig. 4 showed no difference in colours which could be attributed to a strong basal texture achieved while rolling, where most of the grains tend to have their [0001] axis nearly parallel to the normal direction of the sheet as also observed by Zhu et al [23].

The SEM micrographs in Fig. 6 (a-c) contains zinc intermetallic between the grain boundaries as a result of the low precipitation events that occurred during ageing because of the lack of solute precursors to further form precipitates. This is further supported by the presence of precipitate free zones (PFZs) that formed near the grain boundaries as seen in Fig. 6 (e and f).

Although, no strength contributions were observed in the non-solution treated samples due to lack of solute dissolution in the matrix as shown in Fig. 6 (d-f). On comparing with Fig. 7, there is an overall increase in the strength of the alloy due to fine coherent precipitates that were formed from solution treated samples on ageing. Therefore, the solution heat treatment has helped dissolved some solutes into the metal matrix, which after ageing the alloy form a higher amount of precipitates with a smaller size that cannot be observed by SEM, but which do contribute to the hardening achieved by the alloy.

TEP measurements from Fig. 8 showed a decrease in conductivity as ageing time increases with a remarkable difference between 0-24 hours and 24-48 hours of ageing. The first 24 hours had a total decrease of -316 nV/°C whereas the second 24 hours showed a decrease of -17nV/°C, making a total of -333nV/°C; therefore it is likely that most of the solutes in solution might have precipitated without anything left to keep forming the second phase particles. In addition, relative TEP measurements for solution treated samples showed a significant decrease in conductivity, which can be attributed to the better precipitation events arising from higher amount of solutes found in solution. The marked difference in conductivity observed between 24-48hours of ageing between the solution treated and non-solution treated was indicative of the ability of solution treated samples to continually form second phase precipitates from solute contained in the matrix.

5. CONCLUSION

The ageing experiments conducted in this project showed that no strengthening effect can be generated in the ZX40 alloy for times less than one hour of ageing without previously solution heat treating the alloy. The solutes dissolved in the matrix after homogenization precipitate on grain boundaries and also formed precipitates within grains leaving few solutes available to form strengthening second phase particles when ageing. The shorter proposed solution heat treatments showed no strengthening effects when aged for one hour at 180°C, therefore it does not prove viable to strengthen during the paint bake process. The use of longer solution heat treatments in order to generate sufficient precipitation and substantial hardening is required, but would not be viable for automotive industries specifically. The strengthening obtained because of work hardening due to deformation processes was reduced when the alloy was solution heat treated and the loss in strength exceeded the hardening acquired during ageing for these particular conditions. Longer solution treating times severely reduced the hardness of the alloy, which was counterproductive if the ageing times are not long enough to exceed the strength acquired by merely deforming the material.

Further ageing experiments could be made with this alloy with different processing conditions to lower the amount of precipitates formed on grain boundaries during processing, hot forming at 400°C could be used to try to keep as much solutes in solution as possible while partial recrystallization in the microstructure occurs, which could help in enhancing precipitation hardening.

6. ACKNOWLEDGMENT

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