Direct Measurement of the effect of cold rolling on β phase precipitation kinetics in 5xxx series aluminum alloys

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Abstract

The aluminum magnesium alloy system has notable attributes, such as a high strength to weight ratio and weldability, but it can become susceptible to sensitization at relatively low temperatures, which can lead to stress corrosion cracking. It is well established that growth of the secondary β phase is temperature driven, however there is little understanding about the role of prior strain in the β phase nucleation and growth process. Understanding the effect of cold rolling will also bring new insight into better thermomechanical treatments leading to a more appropriate temper to improve sensitization resistance. In this study cold rolled AA5456-H116 is observed during in situ transmission electron microscopy heating experiments. The results of this study show the impact of an increased dislocation density, due to cold rolling, on β phase precipitation as well as the effect of misorientation on growth and kinetics. The effect of additional dislocations is also observed to show an increase in precipitate density and a lowering of nucleation temperature attributed to Mg pipe diffusion.

1. Introduction

The 5xxx series Al-Mg alloy system has received considerable attention as an alternative to steel to decrease structural weights and increase overall fuel efficiency due to their high strength to weight ratio and weldability[1]. **These materials are generally used as structural materials in marine, automotive, and aircraft industries as well as food handling and chemical industries [1-4]. As global warming plays a larger part in material selection, further development on Al-Mg usage has been conducted to improve fuel consumption and emissions, as well as increase recycling potential of final automotive components [1-4].** Use of this material in service, however, has been undermined by stress corrosion cracking [5] resulting from sensitization at moderate and even low temperatures [6]. Growth of a deleterious secondary phase, known as the β phase (Al_3Mg_2), during sensitization of Al-Mg alloys has been a problem for in-service naval vessels for many years [7]. Specifically, while exposed to harsh in-service environments, such as sea water, a galvanic couple is formed between the aluminum matrix and the β phase precipitates[8]. This ultimately leads to a preferential dissolving of these precipitates that result in intergranular cracking[4, 8-10]. But it is possible for crack propagation to occur from non-continuous beta precipitates as well[11].

It is well known that the formation of β phase is temperature driven [12-14] but the nucleation and growth mechanisms are not fully understood. It is generally agreed upon that during exposure to elevated temperatures (50-300°C) the Mg segregation begins from the supersaturated solution (>3%Mg or higher[1]), resulting in the formation of a final, stable β equilibrium phase[5,

12, 13]. Hamana et al.[15] observed β equilibrium to form independently during non-isothermal differential calorimetric analysis, indicating that a direct transformation from its metastable precipitate form, β' , was not required. The majority of studies[16-18] have shown β phase precipitation during long term growth periods at elevated temperatures and have observed the formation of this secondary phase occurs at the grain boundaries (GBs), sub-grains, and defects in the material[19]. Some shorter term accelerated studies have also been used at higher temperature ranges and shorter time periods, and were successful at growing β at GBs and intermetallic precipitates[11, 20]. Despite the heat treatment approach, the precipitate formation of this secondary phase occurred at the GBs, sub-grains, and defects in the material[11, 19].

There exists a lack of information about the location of precipitation, such as dislocations or subgrains and GB character, in relation to precipitate size and speed of formation. Carroll et al. [11] observed the effect of Zn additions in AA5083 after short term sensitization and found β precipitate growth on both high and low angle boundaries but misorientation angle dependence was not examined. In a study of AA5182 sensitization by Davenport et al. [21], however, low-angle boundaries were found to be devoid of β phase precipitation. Our recent work [22] utilized TEM and Astar/Nanomegas orientation imaging to examine GBs misorientation dependence in AA5456-H116 during accelerated in situ heating experiments, and found that β precipitates were present on both high angle and low angle GBs, which was consistent with later studies [23]. Those precipitates found at low angle boundaries indicated inhibited growth (all precipitates were small primarily ranging from 250nm^2 to 1000nm^2) while those found on higher angle GBs had grown to much larger sizes $>5000\text{nm}^2$. Initial studies[24] on 5xxx series Al-Mg system suggested that precipitation on the subgrain structure is actually preferred over high angle boundaries in relation to corrosion performance but there is still a lack of information connecting sub-GB density and its effect on precipitate size and density at high angle GBs. The addition of prior strain will affect the GBs character distribution as discussed in previous studies[25-27] by changing the texture and recrystallization behavior and in turn increase the overall density of subgrains.

While various aforementioned studies [5, 12-13, 15-18] discuss β phase formation from a supersaturated solution, little information exists to explain the specific mechanism of formation. There is a clear lack of information between the supersaturation and the stable presence of β in an equilibrium state. The most common formation mechanism suggested by the literature is that Mg precipitates form from super saturated solution, a process which is facilitated by pipe diffusion via dislocations. Goswami et al.[28] observed that a sample of 5083-H131 showed enhanced β phase growth due to a large dislocation density and, consistent with this finding, observed β phase formation in severely plastically deformed material [29]. Specifically, it was found that during ball milling, GBs were enriched with Mg and thus lead to higher levels of sensitization. On the contrary, a study by Tan and Allen[30] used thermomechanical processing to improve corrosion resistance and found that larger dislocation networks and low angle boundaries lead to better sensitization resistance. Early work by Dix et al [24] expressed the effects of cold work on sensitization, showing a thin line between strength maximization and corrosion resistance during material development. It was discussed that despite lower Mg content, with additional cold rolling, a material could sensitize in the same amount of time as a material with higher Mg content. Gronsky and Furrer [31] also suggested that GB precipitation could be encouraged by additions of extrinsic defects. The amount of prior deformation needs to

be observed in more detail to better understand its full effect on β phase precipitation. Besides increasing the dislocation density and thus the nucleation sites and pathways for precipitation, the impact of pre strain on β phase precipitation is still not well known in relation to growth kinetics. The addition of the pre strain in the form of cold rolling should not alter the growth rate but it should produce higher densities of precipitates due to the increased diffusion paths.

While heterogeneous nucleation of the β phase is known to occur at dislocations, intermetallics, and GBs [11,19,20], and is most likely linked with density of dislocations, what remains a challenge is connecting the nucleation and growth behavior to alloy history and processing. In particular, induced strain from cold rolling and resulting GBs character distribution and dislocation density have a distinctive role in defining the nucleation, growth, and distribution of β phase in 5xxx series Al-Mg alloys. A fully predictive understanding of β phase precipitation is not possible without a clear picture of the role of GBs character in the nucleation and growth mechanism. Using a combined approach of in situ TEM and precession electron diffraction [22] new insight into the effect of prior strain on the onset of β phase nucleation and its subsequent growth is presented. The acquisition of real time video reveals the time, temperature, location and kinetic growth rates of the precipitates and highlights the role of various dislocation densities at the initial onset of β phase nucleation. The results of this work help paint a more complete picture of the nucleation and growth behavior of β phase growth during strain-producing, in-service conditions.

2. Experimental

2.1 Sample Preparation

Aluminum alloy 5456-H116 (5%Mg) was supplied by Alcoa (Alcoa Center, Pa) for this study. Rectangular strips (0.5cm x 0.25cm x 0.635cm) were cut from the bulk (1/4 inch plate) and cold-rolled to 30% and 50% reduction parallel to the rolling direction of the H116 treatment. Rectangular cross-section coupons (2.5cm x 1.2cm x 0.635cm) looking into the rolling direction were cut from the bulk 5456- H116 material (H116) and rolled samples. The coupons were thinned to final dimension of 25mm x 12mm x 0.1mm by mechanical polishing and 3 mm diameter disks were punched. The disks were then polished to 50 microns thickness and ion milled to electron transparency using a Fischione ion mill. Samples were heat treated in a JEOL 2100 Lab6 TEM using a Gatan heating holder at a ramp rate of 0.5° per second up to 300°C and held there for 5 minutes. All experiments were recorded in situ at 10 frames per second using Debut digital screen capture software using a Gatan Orius 832 fiber optic 10.7 megapixel ccd detector. Post-annealing precession diffraction analysis in regions of interest (GBs, dislocation networks) was performed using Nanomegas ASTAR™ orientation imaging as described in section 2.2.

2.2 Precipitate Characterization and GBs Analysis

The Nanomegas ASTAR™ system was used to acquire the misorientation of GBs with β phase precipitates. The system controls the scan coils of the TEM and allows for nanobeam diffraction patterns to be taken across the desired viewing area, similar to electron back scatter diffraction in a scanning electron microscope [22, 32, 33]. Traditional orientation imaging in a scanning

electron microscope is usually conducted using Kikuchi lines while orientation via the Nanomegas ASTAR™ system uses nanobeam diffraction patterns. These observed diffraction patterns are matched to the theoretical diffraction patterns generated from a crystal file indexing the crystal orientation. The Nanomegas ASTAR™ software then yields an inverse pole figure map with the corresponding indexed diffraction patterns at each pixel of the scanned area. An example of this process can be viewed in the supplementary section of this manuscript. While this technique is useful for gaining misorientation data it does lack the ability for finding the boundary plane.

2.3 Precipitate Growth Kinetics Analysis

As described previously, video was collected using Debut digital screen capture software at a frame rate of 10/second using a Gatan Orius 832 fiber optic 10.7 megapixel CCD detector. Images were taken every 10 seconds from the video data starting from 10 seconds prior to the first noticeable signs of nucleation until the 5 minute hold at 300°C was complete. Precipitate analysis was conducted using the ImageJ software package to measure the size of the precipitate at each respective time. These results were then compiled and plotted with all data points normalized with respect to starting nucleation time. The activation energy required for precipitation before and after 300°C were also calculated using the Arrhenius equation. The radius of the particles were calculated from the measured area, and the slope of Ln(Rate) vs. 1/T was used to find the activation energy.

3. Results

3.1 Effect of rolling reduction on β phase precipitate density and size

The addition of extra strain from cold rolling had a large impact on the number density of beta precipitates both within grain matrices and at GBs. This is evident in Figure 1, which shows images of annealed, 0% reduced sample at 20Kx magnification and an annealed, 30% reduced sample at 30Kx magnification. It is clear that there is a large difference in the overall density of precipitation. The 0% reduced samples tended to have more sporadic coverage over the entire area of the sample, whereas the 30% reduced samples had more uniform coverage at GBs and within grain matrices. Finally, the connectivity of the β phase along the GBs was much more uniform in the pre-strained samples than the H116 samples, having smaller distances between precipitates in the rolled samples (figure 1b).

Figure 1: TEM bright field image of H116 after in situ heating experiment at 20kx magnification (b) TEM bright field of 30% reduced sample after in situ heating at 30kx magnification

3.2 Precipitate nucleation and growth

Direct visualization of precipitate growth was observed during in situ TEM heating experiments. Bright field images were taken during in situ annealing showed precipitate evolution at various rolling reductions in figure 2. Due to the high difficulty of predicting where the precipitation

would take place the area of observation was chosen on criteria of general sample quality and number of visible boundaries. Also once the heating experiments were carried out the samples were deemed useless and retrials were not possible due to microstructural evolution upon dissolution. Videos can be found in the supplemental section.

Figure 2: Example of precipitate growth during in-situ heating experiment of 30% reduced sample (a-f). Initial appearance of GB at Time: 208s and Temperature: 141°C (a). First appearance of precipitation at Time: 216s Temperature: 207°C (b). Continued growth at Time: 241s Temperature: 228°C (c), at Time: 281s Temperature: 264°C (d) and at Time: 310s Temperature: 288°C (e). Precipitate growth near completion of experiment Time: 600s and 300°C (f).

Precipitate growth rates were plotted and compared in figure 3. In both the H116 and 30% reduced samples only one precipitate grew within view, both of which occurred on high angle (HA) boundaries. The 50% reduced sample had two HA (labeled 1 and 2) as well as one low angle (LA) boundary precipitate. Precipitate growth rates increased with additional rolling reduction; nuclei in samples with greater rolling reduction were observed to grow faster than those observed in the H116 samples. Growth rates were also found to vary depending on the misorientation of the GBs on which the precipitate grew. While it is difficult to directly compare growth rates across precipitates grown in different samples, figure 3 was used with the x axis normalized with respect to the starting time of the precipitates with point (0,0) being 10 seconds before initial nucleation occurred for any precipitate. This offset allowed for closer comparison of the rates between samples as though the precipitates were all grown in the same sample. The 300°C bar in figure 3 represents a general range using the fastest and slowest time required to achieve the temperature.

Figure 3: Plot of precipitation rates (Precipitate size (nm²) vs. Time (s)) for all samples.

Figure 3 demonstrates the large variation between the rates of nucleation and the precipitation growth rate as a function of prior strain and GBs misorientation. It should be noted that noise present in the growth rate data can be attributed to slight changes in image contrast during in situ annealing, which led to, in some cases, precipitate size measurement deviations of +/- 5%. Immediately noticeable was the stagnation that occurred in cold rolled samples once they reached the 300°C hold temperature, denoting a nucleation and growth transition around 300°C, which will be discussed later. It was also evident that the nucleation stage for the H116 sample did not occur until 120 seconds after the cold rolled samples began to nucleate. With respect to differences in the amount of rolling reduction or prior strain, the 30% and 50% reduced samples showed signs of nucleation within 30 seconds of one another, with the 30% reduced sample starting earlier, or at a lower temperature, than the 50% reduced sample. The data shown in figure 3 was normalized and the nucleation occurs before the heat treatment reaches the 300°C isothermal hold. A dramatic difference is observed in the nucleation temperature between the H116 samples, in which nucleation was first observed at 265°C, and the 30% and 50% reduced samples, in which nucleation was first observed at 191° and 225°C, respectively.

With respect to misorientation, the growth rate of the precipitates on the low angle boundary began before the high angle but had a slower growth rate in comparison as seen in Table 1. Figure 3 also details the size vs. time of precipitates with respect to misorientation angle. For a precipitate grown on a 45° boundary in an H116 sample, nucleation begins at ~265°C and remains sluggish until the 300°C hold temperature is met. Once at 300°C the precipitate growth rate increases and remains steady, reaching a size of ~6000nm². In comparison, initial nucleation of a precipitate on a 20° boundary in the 30% reduced sample is much faster than that of the H116 sample before the 300°C hold is reached, and continues to grow up to a size of 8800nm². Two precipitates measured on two different 60° boundaries, and one precipitate on a low angle boundary (misorientation angle of 5°), were measured in the 50% reduced sample. The first precipitate to nucleate was that found on the low angle boundary, followed by one on a high angle boundary at a triple point, and finally precipitation occurred on the second high angle boundary, also close to a triple point. In the case of these three boundaries, each of the nucleation events began within 10 seconds of the previous one; within 30 seconds, all precipitates had nucleated.

A transition between the nucleation and the growth was observed between the samples; the effect of boundary misorientation and prior strain/rolling reduction on this transition is summarized in Table 1. An immediate observation made was that an increase in rolling reduction did increase the rate of β phase growth. It was also noted that not only did the samples that were cold-rolled nucleate faster, but also, they reached the growth stage first. The rolled samples nucleated during the ramp up to 300°C and once the sample reached 300°C the growth mechanism took over and the precipitate growth slowed and stabilized. The H116 sample grows at a similar rate as the rolled samples did during the ramp up to 300°C. During the nucleation regime the rolled samples have increased slopes for the precipitates grown on high angle boundaries vs low angle. The rates for the two high angle precipitates in the 50% reduced sample are similar while the 30% reduced sample is slightly faster. The precipitate found on a low angle boundary in the cold rolled sample, however, grew very slowly (~75% slower). Additionally, the precipitate in the H116 showed signs of both later/delayed nucleation as well as a slower growth rate. When the rolled samples are observed during the 300°C isothermal hold for 5 minutes the overall observation is that the rate of growth decreases or comes to a halt for the rolled samples.

Sample	Nucleation temp	Final size (nm ²)	Nucleation rate (nm ² /s)	Growth rate (nm ² /s)	Max rate before or after 300°C	Activation energy before 300°C (KJ/Mol)	Activation energy after 300°C (KJ/Mol)
H116 45°	265°C	6310	6.5 ($\pm$ 0.9)	15.7 ($\pm$ 0.97)	After	61.08	68.10
30% reduced 20°	191°C	8819	29.7 ($\pm$ 3.5)	11.2 ($\pm$ 0.33)	Before	22.70	136.21
50% reduced 60° (1)	233°C	2547	25.0 ($\pm$ 1.5)	3.6 ($\pm$ 0.34)	Before	26.29	136.21
50% reduced 60° (2)	242°C	3145	22.8 ($\pm$ 2.8)	0.27 ($\pm$ 0.09)	Before	39.33	113.51
50% reduced 5°	225°C	515	5.9 ($\pm$ 0.8)	0.24 ($\pm$ 0.015)	Before	22.34	113.51

Table 1: Summary of rates for H116 and rolled samples

The resulting activation energies are shown in the final two columns of the table. The activation energy for the H116 sample did not change significantly before or after the 300°C hold and only

increased slightly afterwards coinciding with the steady continued growth after 300°C. The rolled samples, on the other hand, had a significantly lower activation energy before 300°C and a much higher activation energy after 300°C. This agrees well with the rolled samples showing faster growth at lower temperatures while having halted growth at 300°C. As the process continues over time, more Mg segregates to the GBs, leading to higher levels of Mg saturation at the boundary and ultimately a slowed growth. A higher activation energy was calculated in this regime.

3.3. Precipitate distribution with respect to GBs misorientation

Precipitates grown during in situ experiments were measured after annealing to compare size (nm^2) and misorientation angle (degrees) for the three different rolling reductions: 0% (H116), 30%, and 50%. Size, as mentioned above, was measured using Image J, while GBs misorientation was calculated via automated crystal orientation mapping using the Nanomegas ASTARTM system using a method we described previously [22]. An example of this suite of data and images is shown in figure 4, below.

Figure 4: Before and after images of in situ heating experiments with Nanomegas scans of H116 (a -c) 30% reduction (d-f) and 50% reduction (g-i).

A distribution of precipitate size as a function of misorientation angle for all three rolling reductions is shown in figure 5. Each data point in the plot represents a measured value for a single precipitate; 42 GBs were analyzed in the H116 condition, while only 20 boundaries were analyzed in the 30% and 50% reduced samples to achieve the same number of precipitates measured. In the plot, the H116 and 50% reduced samples appear to have fewer precipitates between 20 and 35° misorientation compared to the 30% reduced but this can be attributed to the random selection of boundaries. The majority of precipitates found during the accelerated heating experiments were located on low angle boundaries. A trend similar to previous work [22] was found in that the precipitates grown on low angle boundaries are smaller than those grown on high angle boundaries, which largely exhibited uninhibited growth. The key observation taken from the data shown in figure [5] is the lack of an impact of rolling reduction on the overall precipitate size. The rolled precipitates show the same trend as the H116 samples in that low angle boundary precipitates remain small while high angle precipitates can grow larger. What is also noticeable is that the rolled samples show a larger range of sizes per misorientation. At 45° misorientation for instance sizes range from a few 100nm^2 up to 4000nm^2 and everywhere in between. It is evident from the plot that increasing misorientation angle did not always lead to larger precipitates illustrated in figure 5b. Figure 5c shows the average precipitate size for the low angle ($<15^\circ$) and high angle boundaries ($>15^\circ$) vs. cold rolling reduction. The 30% reduction shows much smaller average size with the H116 and 50% reduced samples at about the same.

Figure 5: Plot of size (nm^2) vs. misorientation angle (degrees) of precipitates (a). Bar graph of average precipitate size (nm^2) vs. misorientation angle (degrees) (b). Average precipitate size (High and low angle) vs. rolling reduction (c).

4. Discussion

Precipitate growth rates increased with rolling reduction; nuclei in samples with greater rolling reduction were observed to grow faster than those in the H116 samples. Growth rates were also found to vary depending on the misorientation of the grain boundary on which the precipitate grew. According to previous results [22] it would be expected that as the misorientation angle increases the size of precipitates would increase as well. While it is true that larger misorientation angles have the ability to accommodate larger precipitates, a high number (in comparison to the H116) of smaller sized precipitates were also found in the cold rolled samples at high angles. This can be attributed to the available amount of Mg in the grain. The increase in precipitation sites within the grain and at the GBs takes away from the total available Mg, thus leaving fewer available solute atoms leading to smaller sized precipitates. The comparison between rolling reduction and precipitate size shows that the increased dislocation density does not always yield larger precipitates. The cold rolled boundaries do however follow the same observations seen in the H116 samples, which are that the low angle precipitates have inhibited growth and the high angle boundaries can accommodate larger precipitates agreeing with the previous study[22]. While the average size of the precipitates did not increase, there was a noticeable increase in the number density of precipitates and thus coverage along the grain boundary indicating a higher degree of sensitization also seen in previous literature[34]. For similar reasons as above deformation from cold rolling yielded more available nucleation sites for β to form and thus the larger number density commonly seen in other systems[35]. These dislocations can also lower the activation energy of precipitation at the grain boundaries which most likely attributes to the increase in more continuous precipitation found at the grain boundaries in the rolled samples.

As a result of the increase in diffusion paths and nucleation sites caused by the higher dislocation density, the precipitates were found to be small in size, but higher in density. The finite number of free Mg atoms within the grain is thought to have diminished faster due the increased nucleation sites yielding smaller precipitates but overall more Mg segregation. As seen in previous studies [29, 36, 37] increasing the dislocation density increased the overall degree of sensitization in materials, perhaps due to the larger number of nucleated secondary phases. This finding is similar to other studies which show precipitate refinement and increased number density [38] as well as smaller precipitates with smaller precipitate spacing [39] in pre strained samples. While it has been suggested that a concept of hard impingement and extended volume can occur in this alloy system [40], β phase growth as monitored in the experiments presented herein did not follow that mechanism at this temperature regime and accelerated timescale. The β phase particles remained discrete, taking on a saw tooth pattern along the GB (figure 1 b).

It stands to be noted that a majority of the precipitation found in this study occurred at low angle GBs. It is generally discussed that low angle GBs possess low energies and degrees of segregation which allow them to be highly resistant to intergranular fracture. [41]. On the other hand, it has been reported that segregated atoms can have an effect on GB energy [42] and thus increase the energy of the low angle GB, but this does not necessarily lower the cohesive strength of the boundary[43]. This idea can be seen in current tempers (H116, H321, and H128), which have been developed to allow precipitation at intragranular locations rather than at the GBs [44]. Zhang et al. [45] discussed that HAGBs increase overall DOS while low angle GBs hinder DOS; moreover they discuss that misorientation has a significant impact on sensitization. In comparison, the results of the precipitation studies presented herein show that the low angle

GBs do indeed act as nucleation sites, but as the heating process continues, high angle GBs accommodate larger precipitates. This is most likely caused by the low angle GBs only accommodating a precipitate up to a finite size whereas the high angle boundary precipitation is uninhibited as shown in this and previous work [22].

β phase formation is temperature driven [12-14] and this phenomena is altered by the presence of prior strain. Specifically, the temperature for nucleation to begin was drastically lowered in the cold rolled samples. The main contribution of the increased dislocation density appears to be a lowering of the overall nucleation temperature and thus more Mg diffusion at lower temperatures. This is shown by the results with the rolled samples having a 30-70°C drop in initial nucleation temperature as well as a lower initial activation energy. These results follow previous studies which show increased dislocation density can lead to lower temperature diffusion [46] brought on by pipe diffusion. As the theory of pipe diffusion via dislocations describes [47] at higher temperatures pipe diffusion has a negligible effect on segregation but at lower temperatures the activation energy for diffusion to begin is greatly lowered. This is directly shown in the precipitation of the reduced samples and their lower activation energies at lower temperatures. While pipe diffusion accounts for the decrease in nucleation temperature as well as increase of nucleation sites the increased precipitation at lower temperatures may be attributed to another factor as well. Due to the higher level of deformation on top of the H116 temper it may be possible for the GBs to be at non-equilibrium states increasing their energy and free volume [48] but on the other hand a severe level of deformation is not likely at these rolling reductions and the changes should be primarily attributed to pipe diffusion.

The comparison between the H116 and the rolled samples showed that the precipitate growth rate was sped up due to the cold rolling. A comparison between the high angle precipitates in the rolled conditions showed very similar growth rates overall despite the additional rolling reduction suggesting diminishing returns above 30% reduction for this alloy. The precipitates at the low angle boundaries were the first to nucleate and grow but did have the slowest growth rate. The key difference between samples is when in which the majority of the growth occurred in the samples. The nucleation and growth of the rolled samples was well completed before the H116 samples precipitate nucleation began. Once the higher temperature of 300°C is reached and held the precipitate growth in the rolled samples begins to slow compared to the H116 sample which tends to have a more steady growth rate. This observation is consistent with the higher calculated value of activation energy after 300°C, consistent with a notion of saturation, with little growth occurring after this temperature. Along with an increased growth rate the rolled samples had many more precipitates form in the same time as the H116, owing to the high density of dislocation nucleation sites. This is in agreement with the idea that pipe diffusion can enhance diffusivity at lower temperatures as well as follows previous assumptions [29,49] that the growth rate is enhanced which is discussed below.

According to the kinetic growth rates of the precipitates the speed of growth is changed by the amount of dislocations. The nucleation regime in the rolled samples is initiated earlier due to a lowering of the activation energy from pipe diffusion. The alloy system precipitation appears to follow classical nucleation growth theories well. The nucleation regime in the rolled samples was where the primary mass of the precipitate accumulated while in the H116 samples the nucleation was slow but the growth rate increased once higher temperatures were achieved. This difference

can be observed by the strong plateau shown in the rolled samples distinguishing the nucleation regime from particle coarsening regime. Conversely in the H116 samples the particle growth regime yields most precipitation. So the increased dislocation density helped to lower the energy for nucleation to begin as well as increased the speed at which the precipitates grew. The difficulty lies in the fact that the rolled samples are not at isothermal conditions compared to that of the H116 samples. The nucleation and growth rates of precipitates at isothermal vs non-isothermal conditions can be very different [50] which may be adding to the rate discrepancy. Finally there is difficulty in directly comparing the above results as they all start nucleating at different times and temperatures as well as in different samples.

It is apparent that the two regimes of precipitation, nucleation and particle coarsening, can be altered by cold rolling [51, 52]. Similarly as to what is shown by Mei et al.[51] lower degrees of cold rolling can increase nucleation sites aiding in precipitate growth but at very high levels precipitation can be stifled due to lack of solute atoms as well as recrystallization. Another study by Fare et al [52] discussed that recovery of heavily deformed structure and precipitation from super saturated solution can occur at the same time. It was also observed that due to high levels of deformation that the aging process occurred rapidly while hardness levels dropped due to recrystallization. The precipitation of the beta phase in the 5xxx series Al-Mg alloy appears to follow these guidelines. At rolling reductions from H116 to 30% (on top of the H116 treatment) the increase in dislocation density allows for more nucleation sites and faster growth rate but overall smaller precipitates similar to work by Dutta et al [49]. This idea breaks down though once higher levels of reduction are added and the precipitation becomes similar to the H116 condition only with a slightly higher rate. This can be explained by the fact that the above experiments were conducted on thin TEM foils in which the increase in dislocation density at the given temperatures could easily lead to some recrystallization, which is similar to results presented by Drits et al. [53], in which faster recrystallization rates were found in thin films compared to bulk. It has been shown even in bulk Al-Mg alloys with high levels of deformation can undergo quick recovery at high temperatures (345°C) and short times <5min[54]. This agrees well with the rates shown in figure 3. Both the H116 and 30% reduced samples continue to grow steadily after the 300°C hold is reached but the 50% reduced sample has very stagnated growth at that temperature. The difference found in the 50% reduced sample can be explained by the idea that the material with higher reduction levels complete the precipitation process faster, and when exposed to higher temperatures recovery of the deformed structure takes over, behavior which is consistent with the aforementioned studies[51-56]. Again while the 50% reduction plus the H116 treatment used in this work may not be at a deformation level equivalent to severely plastic deformed material the extent of the H116 reduction is not fully known due to manufacturer proprietary information and may place the actual reduction closer to 60-70% or even higher.

5. Conclusions

5.1 Impact of pre strain on precipitate size and density

The results show that an increase in dislocation density via cold rolling has an impact on the overall sensitization of the 5xxx series Al-Mg alloy. The size of the precipitates found samples with elevated degrees of cold rolling were very similar to those found in the H116 samples.

While the size of the precipitates did not change dramatically between the rolled and H116 conditions the density of β phase precipitates did increase, which is attributed to the increased dislocation density (heterogeneous sites). The coverage on the grain boundary was found to be drastically different in the pre-strained samples, with the rolled samples having much less space between nucleation sites compared to the H116 which showed large spans between precipitates.

5.2 Growth rate differences caused by pre strain

An increased rolling reduction did increase the rate of growth of β phase. There was a difference observed in rates due to misorientation angle with high angle boundaries showing faster precipitate growth than found on lower angles. The largest impact due to the cold rolling on β phase growth was that on the lowering of the nucleation temperature. The rolled samples saw a much faster nucleation regime rate which occurred at lower temperatures than the H116 sample. The H116 sample took a longer time to nucleate and grew at a slower rate than rolled samples even when higher temperatures were achieved. **Initial activation energies of the rolled samples were lowered due to increased dislocation density coinciding with the pipe diffusion mechanism.** When higher levels of rolling reduction were used the rate did drop and the material mimicked the H116 sample. This was attributed to some material recovery during the heating process.

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