

EFFECTS OF Mn ON GRAIN BOUNDARY PINNING OF 5083 ALUMINUM ALLOY

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ABSTRACT

Superplastic deformation has a significant industrial application value due to the large elongation, which allows manufacturing parts with complex geometries but happens at elevated temperatures and low strain rates. Therefore, it requires alloys with fine grain size but whose grains tend to grow at processing temperatures. Second-phase particles can promote grain pinning to keep a fine grain size structure during superplastic forming. In 5083 aluminum alloy, Al6Mn particles make grain pinning. There are two types of 5083 aluminum alloy: conventional with manganese range from 0.4 to 1.0 wt.% and superplastic with manganese between 0.64 and 0.86. It was observed in bibliographic research that the 5083 superplastic has a higher chemical concentration of manganese than the conventional one. However, no references were found covering manganese concentration in grain size stability. This work shows grain size evolution at a constant temperature of 5083 alloys with different manganese concentrations. After being submitted at 450 °C for 24 h, the sample without manganese presented ~ 26 μ m grain size; this value decreases to 14 µm with 0.4 wt.% of Mn and 11 µm in samples with composition between 0.6 and 1.0 wt.%. Thus, the most indicated manganese concentration to prevent grain growth during superplastic forming at 5083 alloys is between 0.6 and 1.0 wt.% Remember that other properties besides the grain size must be measured to define better an alloy's optimal chemical composition (e.g., corrosion, wear, and mechanical resistances). Other results on grain growth kinetics are presented in the body of work.

Keywords: Aluminum Alloys, superplasticity, AA 5083, grain pinning.

INTRODUCTION

The mobilization of the governments to achieve the CO2 emission reduction targets determined in international conferences such as COP26 has pressed corporations of all sectors to adopt definitions and strategies concerning the ESG Agenda. It is often reflected in the search for more efficient processes and less polluting raw materials for the industrial environment. In this context, the automotive industry sees the substitution of steel for aluminum alloys in automotive vehicle fairings manufacturing as an alternative.

Aluminum alloys show advantages over steel in reducing CO2 emission because of their lower specific weight, better aerodynamics, and the economy in the assembly of automobiles. The last two factors are related to the feasibility of producing parts with complex geometry that improve aerodynamics and still save time and energy in assembly, reducing the need for

welding and riveting⁽¹⁾. The advantages are even more significant for aluminum alloys with a superplastic character.

Superplasticity is the capacity of certain materials to exhibit high elongation before failure, allowing the manufacture of parts with complex geometry with a reduced number of steps or intermediate heat treatment processes⁽²⁾. Typical superplastic elongations are higher than 300%, but some metal alloys can overcome $5,000\%^{(3)}$.

The phenomenon of superplasticity typically occurs by deformation via grain boundary sliding rather than via dislocation slip. Since grain boundary sliding is a surface phenomenon, it requires fine or ultrafine grain size⁽⁴⁾. However, the phenomenon demands high working temperatures and low strain rates, which are known to induce grain growth due to the prolonged times in elevated temperatures⁽²⁻⁵⁾. So, grain growth kinetics is an essential subject in the superplasticity area.

The equation below describes the isothermal grain growth kinetics of many metallic alloys

$$D = D_0 + k. t^n \tag{A}$$

Where D is the average diameter, D_{θ} is the initial diameter, k is a constant, and n is an exponent that is usually close to 0.5 and depends on the alloy's temperature⁽⁶⁾.

To solve this trade-off, chemical elements in alloy manufacturing keep the grain size small even at high temperatures for a prolonged time. These elements can form stable particles, commonly originating during solidification, that may act as grain boundary pinning⁽⁵⁻⁷⁾. By that, the grain growth rate is reduced to stabilize the grain size even in a prolonged time of tens of hours.

The 5083 SP aluminum alloy, well established in the industry, has superplastic characteristics stretching around 350%. Since its first application in 1986, thousands of components have been produced, and there are several sheet manufacturers of this alloy, mainly in the USA, Europe, and Japan⁽⁸⁾. The primary particle that pins the grain boundary in this alloy is Al6Mn⁽⁹⁾. Therefore, manganese is a critical component for the exhibition of the superplastic phenomenon in that case.

ASTM regulates that manganese concentration in the conventional 5083 aluminum alloy varies between 0.4 and 1.0 wt.%⁽¹⁰⁾. On the other hand, a bibliographic survey showed that the 5083 superplastic aluminum alloy has a narrower range for the Mn concentration, between 0.64 and 0.86 wt.%⁽¹¹⁾. However, no reports explaining the different Mn concentrations for the 5083 SP and conventional 5083 aluminum alloys were found in the consulted literature. Therefore, this work aims to evaluate the influence of Mn concentration on the grain growth kinetics of 5083 aluminum alloy to answer that literature gap.

MATERIALS AND METHODS

Five AA 5083 alloys with different Mn concentrations were produced from primary aluminum and the following master alloys: Al with 35.0 wt.% of Mg; Al with 17.4 wt.% of Mn; and Al with 12.0 wt.% of Si. At first, the primary aluminum was melted and held at 750 °C using a

resistance metal melting furnace, and 15 ppm of Be was added to avoid magnesium oxidation. Then, the master alloys were added and kept for 15 min. After it, the melting baths were degassed using Hexachloroethane, and then they were poured into a water-cooled copper crucible with $127 \times 54 \times 13$ mm. The nominal compositions are presented in Table 1.

| Sample | Mn / wt.% | Mg / wt.% | Si / wt.% |
|--------|-----------|-----------|-----------|
| 1 | 0.0 | 4.6 | 0.3 |
| 2 | 0.4 | 4.6 | 0.3 |
| 3 | 0.6 | 4.6 | 0.3 |
| 4 | 0.8 | 4.6 | 03. |
| 5 | 1.0 | 4.6 | 03. |

Table 1: Nominal chemical compositions of AA 5083 with different manganese concentrations.

The ingots were machined to remove superficial defects and improve the rolling quality. Then, they were submitted to homogenization heat treatment at 500 °C for 8 h. Ingots were hot sheet rolled at 420 °C to 13,75 mm in thickness and cold-rolled at room temperature to 2.5 mm, resulting in 81.8% of work hardening. Next, the sheets were annealed at 350°C for 30 minutes, and they were cut into samples of 1 cm \times 1 cm and submitted at 450 °C for 0 (untreated), 1, 2, 4, 24, and 48 h to investigate grain growth. Finally, the samples were heat-treated at 130 °C for 15 h to decorate grain boundaries with the Mg2Si etchable phase.

After usual metallographic preparation, the samples were etched at an aqueous acid solution containing 10 vol.% phosphoric acid at 50 °C per 15 min. Finally, the samples were observed in an optical microscope. Following the standard ASTM E112-13(2021), the Lineal Intercept Procedure was applied to 5 images at each condition to obtain the grain sizes.

The grain size results were treated in the software R^{\odot} , following the statistical model Analysis of Variance (ANOVA) for one factor, the Mn wt.%, with five levels eq.(B). The hypothesis of residuals normality was evaluated with the Shapiro-Wilk test, and was possible to fit a regression model ⁽¹²⁾.

$$\mu i = \mu + \tau i$$
 $i = 1, 2, 3, 4, 5$ (B)

Two analyses were performed, the first evaluated the effect of manganese concentration on primary grain size, and the second evaluated the grain growth behavior at different times for each alloy composition.

RESULTS AND DISCUSSION

Figures 1 a)-c) show optical microscopy images of some samples before grain growth treatment, and Figures 1d)-f) show images after 48 h of heat treatment. It is observed that the initial grain size decreases with the increase of manganese concentration and that grain growth occurs in all samples, as expected.



Figure 1: MO image in the rolling direction of the selected samples of 5083 alloy chemical etched, the rolling plane is parallel to the page, and the rolling direction is horizontal to the page: a-c) Before grain growth treatment; d - f) After 48 h of grain growth at 450 °C.

In this study, sheets were manufactured with five different manganese concentrations submitted to isothermal grain growth at six other time intervals, totaling 30 samples. Five images were obtained per sample, and four lines were drawn per image to measure grain size. Thus, 600 grain size points were obtained. Figure 2 shows the average grain size as a function of manganese concentration and grain growth time.

Figure 2 shows the grain size curve as a function of manganese concentration before grain growth heat treatment. It is observed that the initial grain size decreases significantly with the increase of manganese concentration. Thus, manganese additions are efficient in refining grains. The correlation between initial grain size and manganese concentration of Al5083 alloy was analyzed. The Shapiro-Wilk test returned a p-value>0.05, so the hypothesis of data normality may be accepted, and regression can be set⁽¹²⁾. The characteristic equation found for the system was:

$$D = 12.810 - 6.446. C_{Mn}^{0.5}$$
(C)

Where D is the diameter, C_{Mn} is the manganese concentration in weight percentage, with adjustment R2 equal to 88% and residuals p-value = 0.78. These results prove the residual normality and adjustment of the experimental model. This equation has a physical meaning up to 3.949% p Mn; above this, the grain size is negative. Once equation (C) has a minimum at 3.947 wt.% Mn, we suggest that further research must be performed with manganese concentration superior to 1.0 wt.% Mn.





Figure 2: Average grain size as a function of manganese of samples of AA 5083 before grain growth heat treatment.

Figure 3 presents curves of average grain size as a function of the grain growth time for samples with different manganese concentrations. First, ANOVA followed by Shapiro-Wilk's test, was performed to assess the normality of the residues. The result of the Shapiro-Wilk test is presented in Table 2. It is observed that all p-value results are greater than 0.05, so the hypothesis of data normality is accepted, and regression can be performed ⁽¹²⁾. The data followed the model proposed in equation A. The values of **D**₀, **k**, and **n** are also presented in Table 2. In all cases, the adjustment of R² for the characteristic equation was greater than 80%, see Table 2. The model adequately describes the system's behavior ⁽¹²⁾. The index **n** was little influenced by manganese concentration. On the other hand, the k constant decreases with the increase in manganese content.



Figure 3: Average grain size as a function of grain growth time of AA 5083 at different manganese concentrations.

| Mn / % | P-value | R ² / % | $D_0 / \mu m$ | k | n |
|--------|---------|--------------------|---------------|------|------|
| 0.0 | 0.2992 | 84.41 | 14.02 | 4.02 | 0.34 |
| 0.4 | 0.1655 | 82.87 | 8.98 | 2.54 | 0.22 |
| 0.6 | 0.9789 | 82.83 | 7.60 | 1.40 | 0.34 |
| 0.8 | 0.614 | 84.13 | 6.80 | 1.73 | 0.29 |
| 1.0 | 0.6134 | 83.55 | 6.49 | 1.73 | 0.30 |

Table 2: Parameters obtained from regression model using equation A.

The grain growth rate curve is represented in Figure 4. For all samples, the grain growth rate decreases over time, as expected, because the larger the grain size, the smaller its growth trend. The samples with manganese addition showed a lower grain growth rate than those without addition. It indicates that the addition of manganese slows grain growth. However, the grain growth rate is very similar between 0.4 and 1.0 wt.% of manganese; thus, additions above 0.4 wt.% will not add extra delay in grain growth. However, the increase in manganese concentration decreases the initial grain size, as discussed above.



Grain growth rate (um/h)

Figure 4: Grain growth rate as a function of grain growth time of AA 5083 at different manganese concentrations.

Figure 5 shows a colormap of the average grain size according to manganese concentration and grain growth time. The blue areas indicate the conditions of refined and thermal-stable grains, which is a beneficial characteristic for observing the superplastic phenomenon. In addition, the alloys with 0.8 and 1.0 wt.% Mn have the best results, which after 48h remain with an average grain size between 10.5 and 12.5 μ m, indicating that their corresponding 5083 alloys are strong candidates to present a superplastic behavior concerning their grain thermal stability.



Figure 5: Color map of the average AA 5083 alloy grain size according to the Mn wt.% grain growth time.

CONCLUSIONS

Metallic alloys must present a refined and stable grain size at high temperatures, among other factors, to exhibit superplasticity. Therefore, it gives importance to this work on the influence of manganese concentration in the 5083 aluminum alloy on microstructural refinement and grain growth kinetics.

Samples with manganese concentrations ranging from zero to 1.0 wt.% were submitted to 81.8% of cold rolling, annealed at 350 °C for 30 min, and thermally treated at 450 °C for 1, 2, 4, 24, and 48 h for grain growth.

It was shown that the initial grain size decreases gradually from 12.77 to 6.48 μ m with the increase in the amount of manganese. Although therefore, the relationship between initial grain size and manganese concentration could be modeled by equation (C), which suggests that additions higher than 1.0 wt.% of manganese can further decrease the initial grain size.

All samples with manganese addition showed approximately equal grain growth rates but were lower than those without manganese. Finally, manganese additions higher than 0.4 wt.% promote grain refinement. Still, above this composition, the addition of manganese does not amplify the phenomenon of grain pinning in ingots manufactured by the methodology of this work.

These results are essential to understanding the effects of manganese composition on grain refinement and thus optimize the alloy's superplastic properties. However, these results should be used cautiously, as other factors may compromise superplastic capacity. For example, manganese additions may promote the formation of coarse second-phase particles that cause cavitation voids that compromise alloy ductility.

Future work is needed to analyze the influence of manganese concentrations greater than 1% on grain size, ductility, and cavitation in 5083 alloys.

ACKNOWLEDGMENTS

The authors thank the following organisations for making this project possible: Alfa Trend Indústria e Comércio Ltda; and ITAEx – Ex-Alunos Apoiando o ITA.

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