ABSTRACT Two different aspects of the thermal stability of grains were studied – (i) thermal stability of grain structure evolution during friction stir processing (FSP), and (ii) thermal stability of grains after FSP. It was concluded that Al$_3$(Sc,Zr) dispersoids are effective in limiting grain growth to ultrafine grained regime (UFG) by stabilizing the microstructure during FSP. The presence of these dispersoids before processing was more effective in refining the grain size than the case in which these dispersoids precipitated during FSP. The mean grain size for these cases were 400±170 nm and 500±247 nm, respectively. Isothermal grain growth study revealed that UFG grain structure was maintained up to 450 °C even after 16 h of annealing whereas most of the UFG alloys reported in the literature show extensive grain growth above 200 °C. To understand the role of Al$_3$(Sc,Zr) precipitates in this alloy, 5086Al-H32 was friction stir processed and subjected to identical annealing conditions. Annealing of FSP 5086Al-H32 at 350 °C for 1 h resulted into abnormal grain growth (AGG). The onset of AGG was observed for UFG sample only after annealing at 550 °C for 1 h. This was rationalized using Humphreys model for AGG [F.J. Humphrey, Acta Mater., 45 (1997) 5031].

1. INTRODUCTION

In the past two decades several grain refinement techniques [1-5] have been developed to refine the grain size to take advantage of Hall-Petch strengthening [6-7]. Polycrystalline materials having grain size below 1 μm (ultrafine grained (UFG) and nanocrystalline) have opened up entirely new domain of research due to their difference in physical, chemical, and mechanical behaviors as compared to coarse grained (CG) materials [8-9]. But, as grain size decreases there is an increase in grain boundary area per unit volume. Assuming a cube shaped grain it can be shown that 50 % reduction of grain leads to an increase in surface area by ~ 16 % and a reduction of 99 % can cause surface area to increase by ~ 3267 %. [10]. If grain boundary energy per unit area of a material is assumed to be independent of its grain size, there will be corresponding increase in total grain boundary energy per unit volume. Hence, grain refinement will always lead to an increase in the free energy of the system thereby making the microstructure unstable. Such grains when subjected to thermal cycle have tendency to grow to minimize their energy by reducing the grain boundary area per unit volume.

Thermal instability of the nanocrystalline [11-15] and UFG [16-24] materials have been an issue and studied by many researchers. Thermal stability of equal channel angular pressing (ECAP) processed UFG Al-3wt%Mg was studied by Wang et al. [25]. They studied the thermal stability of this alloy in the range 443- 803 K. The UFG structure was found to be quite unstable. The recrystallization and grain growth resulted in elimination of UFG microstructure above 550 K. Stability of UFG microstructure up to 700 K was reported by Furukawa et al. [26] in a similar work on ECAP processed Al-5.5Mg-2.2Li-0.12Zr (wt%). Such a high resistance to grain growth was attributed to very fine dispersion of Al$_3$Zr dispersoids. In a similar work on ECAP processed UFG Al-0.2 wt% Zr with grain size 0.7 μm, UFG microstructure was retained only up to 573 K [16]. In another study by Park et al. [18] on accumulative roll bonding (ARB) processed UFG 6061Al, thermal stability was studied for 1 h in the temperature range 373-773 K. UFG microstructure was maintained only up to 473 K. Indranil et al. [21] have investigated the thermal stability of a cryomilled UFG 5083Al alloy. Similar to Furukawa et al. [26] the stability of UFG microstructure was reported up to 673 K. However, such a high level of stability of grains was attributed to the dispersion of particles such as oxides, carbides, and nitrides on the grain boundaries. This brief survey on the thermal stability of UFG alloys indicates that the thermal stability is not very high and use of dispersoids pushes the stability envelop towards the higher temperature range.

The rate of increase of grain boundary area per unit volume is strongly influenced by the mode of deformation. Gil Sevillano et al. [27] showed that rate of generation of grain boundary area per unit volume was maximum for the sample deformed under compression than those deformed either by rolling, wire drawing or torsion for the same level of equivalent strain. It indicates towards the fact that different processing techniques introduce different types of microstructure. Hence, UFG materials
processed via different routes will have different microstructures which would result into different response to thermal treatment. Therefore, thermal stability of UFG alloys processed via friction stir processing (FSP) is of interest in spite of similar studies done on UFG materials processed by other techniques [16-24].

In the present work two different aspects of thermal stability will be addressed. FSP has potential of refining grains as small as 25 nm [28 -30]. But commonly observed grains are larger than 1 μm [31]. Zener pinning mechanism is known to inhibit grain growth. This is realized by the use of precipitates or dispersoids in the microstructure. Precipitates are generally not very effective grain growth inhibitor due to either rapid dissolution or excessive coarsening during FSP. Use of dispersoids largely remains unexplored. In the present work this aspect of grain stabilization to obtain UFG alloy will be addressed. Another aspect is grain growth of UFG alloy after processing.

2. EXPERIMENTAL PROCEDURE

2.1 Processing of the alloys

A twin rolled cast (TRC) Al-Mg-Sc sheet (nominal composition: Al-4Sc-0.8Sc-0.08Zr, wt%) ~ 3.75 mm thickness was subjected to FSP in as-received (here afterwards referred to as TRC-AR) and aged (here afterwards referred to as TRC-Aged) conditions. The aging was carried out at 290 °C for 22 h. It resulted into precipitation of Al₃(Sc,Zr) dispersoids. To evaluate the effectiveness of these dispersoids in inhibiting grain growth during FSP, work hardenable 5086Al-H32 was friction stir processed under same processing condition as TRC alloy. A tool rotation rate of 325 rpm and a tool traverse speed of 8 ipm (203 mm/min) were used to process these alloys. Tool tilt angle was 2.5° and plunge depth was 0.097" (2.5 mm). The tool material was tool steel and tool had concave shoulder and stepped spiral pin profile. The diameter of the shoulder was 12.0 mm. The pin diameter at root and the tip were 6.0 mm and 3.5 mm, respectively. The height of the pin was 2.2 mm measured from the root of the pin.

2.2 Annealing heat treatment for the thermal stability study

For thermal stability study, FSP TRC-Aged and 5086Al-H32 samples were subjected to isothermal annealing heat treatment. FSP TRC-Aged alloy was annealed at 523 K for 1-16 h and at 623 K for 1 h.

2.3 Characterization of the microstructure

Characterization of the microstructure was done by electron backscattering diffraction (EBSD) microscopy using HKL EBSD system fitted on FEI Helios NanoLab 600 FIB/FESEM. Each sample was mechanically polished using water based diamond suspension up to 1 μm grit size and then polishing using 0.02 μm colloidal silica suspension. EBSD was carried out in as-polished condition. Centre of the FSP nugget on transverse cross-section was chosen for EBSD analysis.

3. RESULTS

3.1 Thermal stability during FSP

The microstructure after FSP is shown in Figure 1 for two different starting conditions. The accompanying inverse pole figure illustrates the various crystallographic axes associated with different colors. All these crystallographic directions are parallel to FSP direction. Figure 1a corresponds to TRC alloy processed in AR condition at 325 rpm and 8 ipm (203 mm/min). OIM corresponding to TRC alloy processed in aged condition has been shown in Figure 1b. It can be noticed that FSP of TRC-Aged alloy resulted in a finer microstructure. Quantitative analysis of grain size showed a mean grain size of 0.49±0.25 μm and 0.40±0.16 μm for TRC-AR and TRC-Aged, respectively. The grain size distribution (GSD) histograms for these two conditions have been shown in Figure 2. In both the cases GSD can be represented by theoretical Rayleigh or Louat’s distribution [32] and has been shown in the same figure. It is evident from the GSD plot that some of the grains for FSP TRC-AR were larger than 1 μm. But, almost all the grains were less than 1 μm for FSP TRC-Aged. The GSD histograms show that in both the cases minimum grain size was same. It is an artifact of step size selection during EBSD data acquisition. In both the cases step-size was 100 nm and minimum grain size was found to be 115 nm. A smaller step size may have some impact on the distribution of grain size towards the smaller grain sizes. But it is not expected to change the average grain size and overall GSD considerably.

FSP 5086-H32 alloys showed an average grain size of 1.1±0.81 μm. The cumulative grain size distribution plot for this alloy has been shown in Figure 3 along with the cumulative distribution of TRC Al-Mg-Sc alloy. From this figure, the effect of
dispersoid on the stability of grains during FSP can be noted. FSP 5086Al-H32 alloy had ~ 50 % grains larger than 1 μm whereas TRC alloy had almost all the grains smaller than 1 μm. TRC-Aged alloy showed about 80 % grains below 500 nm. It was about 60 % for TRC-AR alloy.

3.2 Grain growth study

OIM micrographs corresponding to annealing of FSP 5086Al-H32 along with as-processed OIM micrograph are shown in Figure 4. It can be noted that annealing at 250 °C from 1 h to 16 h only resulted in recovery and annihilation of substructure developed during FSP. When sample was annealed at 350 °C for 1 h, abnormal grain growth was observed. Very large grains (~ 100 μm) can be seen in Figure 4d along with very fine grains at the centre of the image. The corresponding cumulative grain size distributions for these four conditions are shown in Figure 5. In AP condition ~ 60 % grains were smaller than 1 μm. On annealing at 250 °C for 1 h, larger grains grew at the expense of smaller grains as evident from reduction of percentage of grains below 1 μm (38 %). But fraction of grains below 1 μm marginally changed after annealing the sample at 250 °C for 16 h. Cumulative frequency curves related to these two conditions also indicate that there was no significant change in the grain size distribution on annealing for these two times. In the specimen annealed at 350 °C, the GSD distribution curve up to 3-4 μm follows GSD distribution curves related to samples annealed at lower temperature very closely and afterwards become flat up to 100 μm. It is indicative of the presence of very large grains due to abnormal grain growth.
annealed at 823 K for 1 h shows considerable grain growth.

Figure 5. Cumulative grain size distribution of FSP 5086Al-H32 alloy in various thermomechanical conditions.

Figure 6. OIM micrographs show the grain growth behavior of FSP TRC-Aged alloy in different conditions; (a) 250 °C (523 K), 16 h, (b) 350 °C (623 K), 16 h, (c) 450 °C (723 K), 16 h, and (d) 550 °C (823 K), 1 h.

Figure 7a shows the variation of average grain size as a function of time and temperature. It can be noted that annealing of samples at 523 K and 623 K up to 16 h did not change the average grain size at all. Although, grain growth was observed at 723 K when annealed between 1 to 16 h the grain growth kinetics was not very fast. The sample annealed at 823 K for 1 h showed a substantial grain growth and very high grain growth kinetics as evident from the slope of the curve. In Figure 7b, thermal stability of FSP TRC-Aged alloy annealed at different temperature for 1 h has been compared with the thermal stability of UFG alloys processed by various other routes. Comparison of the present data shows that most of the UFG alloys have very poor thermal stability and above ~ 473 K UFG microstructure is lost. The FSP TRC-Aged alloy maintained its UFG microstructure up to 723 K.

4. DISCUSSION

As mentioned before FSP has the potential of producing nanocrystalline grains. But, this advantage is lost due to excessive grain growth of refined microstructure during FSP because of high temperatures involved during the process. The thermal cycle a processed volume goes through during FSP is shown schematically in Figure 8. The final grain size depends largely on how much time a processed volume spends above \( T_{\text{min}} \), minimum temperature to induce grain growth. One way of cutting down time spent above \( T_{\text{min}} \) is to increase the rate of cooling as shown by red (curve 1), blue (curve 2), and black (curve 3) lines representing cooling rates in increasing order. These different levels of cooling rates can be obtained by using external cooling media such as liquid nitrogen, copper backing plate, forced chilled air cooling, etc. Another method of reducing the time above \( T_{\text{min}} \) would be to reduce the peak temperature (shown by curve 4). The peak temperature (\( T_{\text{peak}} \)) can be manipulated by controlling the tool rotation rate and/or tool traverse speed. These two strategies have been widely used to stabilize the processed microstructure during FSP. Here, use of a third strategy has been shown to refine the microstructure during FSP as outlined next.

Figure 8. A schematic illustration of the thermal cycle experienced by a particular volume of material during FSP and its effect on grain refinement process.
In the present study, two different scenarios were investigated – (a) precipitation of dispersoids during FSP, i.e., FSP of as-received Al-Mg-Sc which contained Sc in solid solution and (b) FSP in aged condition. The effectiveness of case (a) in grain refinement was lower than that of case (b). Since, in case (a) dispersoids have to precipitate out during FSP, their effectiveness in acting as Zener pinning agent will depend on the kinetics of stable precipitate nuclei formation and also the volume fraction of the dispersoids. For stable particles or dispersoids containing alloys, limiting grain size is given as

\[
\bar{D} = \frac{4d}{3F_r}
\]  

where \(\bar{D}\), \(d\) and \(F_r\) are average grain size in FSP condition, radius and volume fraction of precipitates or dispersoids, respectively. Ignoring the amount of Zr, the present alloy system can be treated as a binary system – (Al,Mg)-Sc. Al-Sc literature shows that depending upon the rate of cooling solid solubility of Sc in Al can vary anywhere from 0.35 wt% (equilibrium cooling) to 0.6 wt% (at a cooling rate of 100 K/s) [33]. If all the Sc in solid solution precipitates out in the form of Al\(_3\)(Sc,Zr) dispersoids, applying the lever rule it can be shown that it will correspond to 0.0168 volume fraction of these dispersoids. Based on the work of Lee et al. [34] and Marquis et al. [35] on Al-Mg-Sc system, the size of Al\(_3\)(Sc,Zr) dispersoids are not expected to be larger than 5 nm. Substituting these values in Eq. (1), limiting grain size \(\bar{D}\) is 0.4 \(\mu\)m. The experimentally observed mean grain size in the case (b) was also 0.4 \(\mu\)m. The measurable coarsening of Al\(_3\)(Sc,Zr) dispersoids takes place only above 573 K, if heated for considerable amount of time. In the case (a), a material volume in the wake of the FSP tool is not expected to be above 573 K for a considerable amount of time. Hence, the dispersoid size should be about 2-3 nm. The works of Fuller et al. [36], Marquis and Seidman [37], and Knipling et al. [38] support this assumption. The mean grain size found in the case (a) was 0.5 \(\mu\)m. Substituting these values (limiting grain size equal to mean grain size and dispersoid size equal to 2 nm) in Eq. (1), the volume fraction of the dispersoids was found to be 0.0053. The estimated volume fraction in this case is lower than that of case (b). This is an expected result. Given the very short duration of FSP, complete precipitation of the dispersoids is unlikely. So, the volume fraction of Al\(_3\)(Sc,Zr) dispersoids would be. Hence, in spite of having smaller dispersoid size in the case (a), lower volume fraction of the dispersoids resulted into a higher limiting grain size. Other noticeable difference due to the presence of Al\(_3\)(Sc,Zr) dispersoids before FSP was higher frequency of smaller grain sizes.

Grain growth study revealed that presence of stable dispersoids like Al\(_3\)(Sc,Zr) can stabilize very fine grain size at temperatures as high as 723 K. Such a high level of thermal stability of grains is hardly observed in any of the previously reported UFG materials except for a report by Ma et al. [39] for Al-4Mg-1Zr alloy. The highly thermal resistant Al\(_3\)Zr dispersoids were attributed for such a high thermal stability of this alloy system. The UFG microstructure was maintained up to 698 K (mean grain size - 0.98 \(\mu\)m at this temperature) in this case. Most of the UFG Al alloys lose their UFG structure above 473 K – 523 K.

The case of abnormal grain growth for particle containing alloys have been dealt with by many researchers, but only the model proposed by Humphrey’s [40] will be discussed here. The condition for AGG is given as

\[
\frac{dR}{dt} - \frac{d\bar{R}}{dt} > 0
\]

where \(\bar{R}\) and \(R\) are mean grain size and size of any grain, respectively, in a polycrystalline material.

\[
\frac{d\bar{R}}{dt} = M\left(\bar{\gamma} - \frac{\gamma}{R} - Z\gamma\right)
\]

\[
\frac{d\bar{R}}{dt} = \bar{M}\gamma(0.25 - Z)
\]

where

\(Z = \frac{3F_r\bar{R}}{d}\)

Here, \(\bar{\gamma}\), \(\gamma\), \(M\), \(\bar{M}\), and \(Z\) are average grain boundary energy, grain boundary energy, grain boundary mobility, average grain boundary mobility, and particle pinning parameter, respectively.

From Eq. (4), for \(Z\geq0.25\),

\[
\frac{d\bar{R}}{dt} = 0
\]

Hence, as per Eq. (2) AGG can take place only if

\[
\bar{R}\frac{d\bar{R}}{dt} > 0
\]
i.e.,
\[ R \frac{dR}{dt} = R M \left( \frac{\gamma}{R} - \frac{\gamma}{R} - \frac{Z \gamma}{R} \right) > 0 \]

Simplification of this expression leads to
\[ R < \frac{d}{dR} \left( 1 - \frac{1}{X} \right) \]

where
\[ X = \frac{R}{\gamma} \]

The variation of \( R \) with \( F_v / d \) has been shown in Figure 9. It depicts the region of normal grain growth, AGG, and no grain growth. Hence, AGG can take place when particle pinning parameter \( Z \) lies between 0.25 and 1. Parameter \( Z \) is a function of temperature. For the present case it was calculated for all the annealing temperatures. To calculate \( Z \), volume fraction of dispersoids, mean grain size (radius), and dispersoid radius were needed. The volume fraction calculation was done at each temperature based on the solvus curve related to Al-Sc reported by Roys et and Ryum [33]. The procedure of volume fraction calculation at each temperature was same as outlined in the discussion on thermal stability during FSP. The mean grain size radius was calculated from the EBSD analysis. The dispersoid radius was taken from the work of Jones and Humphreys [41] on Al3Sc dispersoids coarsening as a function of temperature. The calculated \( Z \) values are listed in Table I.

### Table I. Values of different variables used in the calculation of particle pinning parameter, \( Z \).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Dispersoid size (nm)</th>
<th>Solubility of Sc in Al, wt%</th>
<th>Dispersoid volume fraction</th>
<th>Mean grain size (radius)</th>
<th>Particle pinning parameter, ( Z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>5</td>
<td>negligible</td>
<td>0.0168</td>
<td>0.26</td>
<td>2.7</td>
</tr>
<tr>
<td>350</td>
<td>5</td>
<td>negligible</td>
<td>0.0168</td>
<td>0.26</td>
<td>2.7</td>
</tr>
<tr>
<td>450</td>
<td>9</td>
<td>0.034</td>
<td>0.0159</td>
<td>0.26</td>
<td>1.4</td>
</tr>
<tr>
<td>550</td>
<td>47</td>
<td>0.125</td>
<td>0.0133</td>
<td>0.26</td>
<td>0.22</td>
</tr>
</tbody>
</table>

The calculated \( Z \) values are superimposed on the grain stability map shown in Figure 9a. From the values of \( Z \), it is clear that it decreases with increase in temperature. A similar calculation by Charit and Mishra [42] for precipitates/dispersoids in FSP UFG Al-Zn-Mg-Sc alloy showed a decrease in \( Z \) with the increase in temperature. The \( Z \) values at 523 K and 623 K fall into no growth region of the grain stability map. The grain size histogram corresponding to annealing at 523 K and 623 K for 1 h are shown in Figure 9b. Clearly, both the histograms superimpose each other completely. Also, mean grain size in these two conditions were same as in as processed condition. The \( Z \) value for the sample annealed at 723 K for 1 h also lies in the no growth region but this time it is very close to upper limit (\( Z = 1 \)) of the AGG region. Ideally, there should not be any grain growth in this sample too since it is a part of no growth region. The mean grain size in this case was 0.74 μm. It can be attributed to lowering of Zener pinning pressure due to coarsening of Al3(Sc,Zr) dispersoids. The grain size distribution histogram is shown in Figure 9b. An increase in relative frequency of grains in the range 1.5 to 2.0 μm can be noted. But still grain size distribution is same as those annealed at lower temperatures. If the sample is annealed at 723 K for longer period of time, it will cause further coarsening of Al3(Sc,Zr) dispersoids. That may result in reduction of \( Z \) value further and consequential shift in the position of datum point towards the AGG region and may eventually become part of AGG region as shown by a blue colored open circle. In such a scenario the sample should show abnormal grain growth. The analysis of grain size distribution histogram of the sample annealed at 723 K for 16 h shows a bimodal grain size distribution as shown in Figure 9d. Apart from a peak in UFG regime, the presence of another peak at ~ 1 μm can also be noted. The bimodal grain size can be considered as an onset of AGG. The sample annealed at 823 K for 1 h showed AGG. It is evident not only from the OIM micrographs shown in Figure 6d but also from the grain size distribution histogram shown in Figure 9e. Apart from the presence of multiple peaks, some grains larger than 10 μm can also be noted in Figure 9e. It should be noted that ideally AGG for this condition should not have been observed since the \( Z \) lied in the normal grain growth region on the grain stability map. Since, the grain stability map was constructed under the assumption that all the grain boundaries had same mobilities and the same grain boundary energy, in real material the deviation from this ideality is quite possible. Hence, to represent the observed behavior of the present alloy system, the curve corresponding to \( Z = 0.25 \) (left side red curve) was shifted towards left to cover the pink circle representing \( Z \) of the sample annealed at 823 K for 1 h. By same amount this red curve was shifted towards right. Similar exercise was done for the curve corresponding to \( Z = 1 \) (right side red curve).
The red curve was shifted by the same amount as in the left hand side red curve. Hence, for real system instead of a line, a band can be used to explain such deviations from ideality.

![Graph showing grain size distribution](image)

**Figure 9.** (a) A grain stability map and (b-e) comparison of the predictions made by this map with the experimentally observed grain growth behavior.

5. **CONCLUSIONS**

The following conclusions can be made based on foregoing discussion:

I. Dispersoids like Al₂(Sc,Zr) are effective means of inhibiting the grain growth during FSP.
II. The presence of the dispersoids before FSP is much more effective for Zener pinning than their precipitation during FSP.
III. Post-FSP annealing heat treatment showed a very high thermal stability of UFG microstructure. UFG microstructure was maintained up to 450 °C (723 K).
IV. Humphrey’s model for abnormal grain growth can be utilized to explain the thermal stability of the present alloy system.

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7. REFERENCES