Reactive mechanism and mechanical properties of in-situ hybrid nano-composites fabricated from an Al–Fe$_2$O$_3$ system by friction stir processing

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ABSTRACT

In-situ Al/(Al$_3$Fe$_4$ + Al$_2$O$_3$) hybrid nano-composite was fabricated using reactive friction stir processing (FSP) by introduction of Fe$_2$O$_3$ powder into the stir zone of rolled AA1050 aluminum alloy. Composite reinforcements were produced in-situ by exothermic reaction of Al and Fe$_2$O$_3$ that initiated by hot working characteristics of FSP. However, the existence of intermediate phase (Fe$_3$O$_4$) suggests that the reaction was not completed due to short time of FSP. EBSD results showed that the matrix mean grain size decreased to 8 and 3 μm after FSP without and with introduction of powder, respectively; this was also associated with the marked increase in HAGB. The fabricated nano-composite exhibited superior hardness (45 HV) and ultimate tensile strength (~171 MPa) compared to those of the base and FSPed alloy with no powder addition. Formation of in-situ reinforcements and grain refinement acted as major and minor contributors to enhancement of mechanical properties (hardness and ultimate tensile strength), respectively.

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1. Introduction

Reactive friction stir processing (FSP) has been reported in recent years [1–5]. In this case, the FSP is associated with a reaction between the plasticized stir zone (SZ) of the work piece and introduced solid [4] or gas [3]. Although FSP is done in a short time, the generated heat and complex flow of material can initiate and proceed exothermic reactions. One famous exothermic reaction in welding and surface engineering is thermitic that occurs between aluminum and an oxide of less reactive metal, forming stable Al$_2$O$_3$. Alumina (Al$_2$O$_3$) particles serve as effective reinforcements in aluminum matrix for improving mechanical properties. There have been attempts to fabricate Al/Al$_2$O$_3$ composite by in-situ techniques involving the reaction between Al and a metal oxide [6–8]. Recent researches [9,10] showed that aluminum matrix composites reinforced by in-situ formed Al$_2$O$_3$ nanoparticles could be fabricated by the combination of FSP and thermitic reaction. Various aluminum matrix composites reinforced by Al$_2$O$_3$ nanoparticles were fabricated by FSP using Al–CeO$_2$ [9], Al–TiO$_2$ [4,5,11], and Al–CuO [12] systems, where Al$_2$O$_3$ particles formed in-situ by reactive mechanisms.

For many oxide-aluminum displacement reactions, the reduced metal may react exothermically with Al to form intermetallic compound, which in turn rises the system temperature [13]. However, the exothermic reactions could not proceed sufficiently even after four passes of FSP with 100% overlapping [6,10,14,15]. The Fe$_2$O$_3$/Al mixture is a well-known thermite system producing an exothermic reaction regarding the following stoichiometric compositions:

$$8\text{Al} + 3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{Al} + 3\text{Al}_2\text{O}_3 + \text{heat}$$  (1)

The final phases, Al$_2$O$_3$ and Fe$_3$Al intermetallic compound, are formed by an in-situ chemical reaction in which Al reduces iron oxide [16]. This stoichiometric reaction is proposed for the thermite mixture when a powder mixture of 8Al–3Fe$_2$O$_3$ (given in mol%) is prepared (i.e., mass ratio of Fe$_2$O$_3$/Al ~2.2), though non-stoichiometric compositions may manipulate the final products [17]. The in-situ-formed Al$_2$O$_3$ and Al–Fe intermetallic products are of high strength and can contribute to strengthening, when they act as fine reinforcements with homogenous distribution within the Al matrix [16]. The objective of the present study is to elucidate the formation mechanism of Al$_2$O$_3$ and Al–Fe intermetallic in Al–Fe$_2$O$_3$ system induced by FSP. In addition, the mechanical properties of the fabricated composites are evaluated.
2. Materials and Methods

A 5 mm-thick sheet of AA1050 was selected due to its high Al content (>99%); this is considered to be suitable for logical interpretation of structures and properties of the resulting composites from Fe$_2$O$_3$-Al system. The rolled sheet was supplied by Arak Aluminum Co., Arak, Iran and its nominal chemical composition presented in Table 1. The sheet was cut to prepare work pieces with a length and width 210 and 70, respectively. A groove with 3.5 mm depth and 1.4 mm width was machined in the middle length of each work piece and filled by Fe$_2$O$_3$ powder (>98% purity, mean particle size of ~1 μm). In order to encapsulate the powder and to prevent scattering during FSP, the groove was sealed by traversing a pin-less tool with 10 mm shoulder diameter using rotational (w) and traverse speeds (v) of 1120 rpm and 125 mm/min, respectively. FSP was performed using a vertical milling machine employing a H13 steel tool with shoulder diameter of 18 mm, pin diameter and height of 5 and 4 mm, respectively. The processing parameters were w = 1400 rpm and v = 40 mm/min. Al work pieces were subjected to four passes of FSP with 100% overlapping, i.e. four passes of FSP were conducted along the same path. For comparison, FSP was applied on a work piece without introduction of Fe$_2$O$_3$ powder using the same processing parameters and conditions.

Specimens for microstructural studies were prepared by cutting sections transversely to the FSPed work pieces and then ground down and polished on the cloth using diamond paste. Keller reagent (2 ml HF + 3 ml HCl + 5 ml HNO$_3$ + 190 ml H$_2$O) was used for etching the specimens. Microstructural studies were conducted by optical (OM; Olympus GX51), scanning (SEM; Jeol JSM-7600F) and transmission electron microscopy (TEM; Jeol 2000FX). The SEM was linked to an energy-dispersive spectroscopy (EDS) and electron back scattered diffraction (EBSD; Oxford Instruments, X-Max) detectors. For the microstructural studies by EBSD, standard metallographic procedures (automatic grinding and polishing) were followed by colloidal silica polishing for 45 min. EBSD data were then processed using Mambo and Tango software to plot misorientation distribution curves. A clean-up with a grain tolerance angle of 5° and minimum confidence index of 0.1 (CI > 0.1) was applied to re-index the data points. Low-angle grain boundaries (LAGBs) were defined at misorientations in the range of 3 to 15° (bright contrast in EBSD images), while boundaries with higher angles were considered as high-angle grain boundaries (HAGBs, dark contrast in EBSD images). An X-ray diffraction unit (Rigaku Ultima IV) was used to identify the phases of the fabricated composites. For TEM analysis, thin sections of ~40 μm thickness and 3 mm diameter were prepared from the center of the SZs. These sections were dimpled by Gatan dimpler and subsequently thinned to electron transparency using a Gatan precision ion mill (Gatan PIPS II, Model 695). Ion milling has been generated within the SZ probably due to an exothermic reaction. Grain refinement was enhanced by the introduction of Fe$_2$O$_3$ particles into the SZ (Fig. 2c). Flow pattern with relatively small spacing in the SZ could be an indication of near through mixing (Fig. 2c).

Low-magnified cross-sectional images of the SZs of FSPed AA1050 with and without Fe$_2$O$_3$ powder are shown in Fig. 1. Microstructural studies exhibited no coarse agglomeration of nanoparticles in the SZ. It should be noted that the SZ introduced with Fe$_2$O$_3$ powder is bigger in size than that without powder; this is an indication that extra heat has been generated within the SZ probably due to an exothermic reaction.

Fig. 2 shows the microstructure of the base alloy (Fig. 2a), FSPed specimens without (Fig. 2b) and with (Fig. 2c) Fe$_2$O$_3$ powder at higher magnification. SZ grains were found to be refined after FSP (Fig. 2b). Grain refinement was enhanced by the introduction of Fe$_2$O$_3$ particles into the SZ (Fig. 2c). Flow pattern with relatively small spacing in the SZ could be an indication of near through mixing (Fig. 2c).

Fig. 3 shows the typical microstructure of FSPed AA1050 with and without Fe$_2$O$_3$ addition using backscattered electron imaging. Particles with quite uniform distribution were found in the FSPed specimen with Fe$_2$O$_3$ powder (Fig. 3b). Thus, a composite material is fabricated.
Particles in the composite exhibited different contrasts with respect to their matrix (Fig. 4a). According to the EDS point and elemental mapping analyses (Fig. 4a, b, and c), the matrix with dark gray (A), and particles with light gray (B), bright (C), and pale gray (D) contrasts are consistent with Al, Al–Fe compound, iron oxide, and aluminum oxide compositions, respectively.

It should be considered that since C and D particles are smaller than the EDS resolution, their chemical analyses are suggested to be based on qualitative elemental partitioning deduced from X-ray mapping rather than quantitative point analyses. The presence of particles with the mentioned chemical analyses confirmed the occurrence of Al/Fe2O3 reaction. However, reaction was not completed kinetically since iron oxide particles remained in the fabricated composite even after four passes of FSP. Quantitative point analyses of B particles were found to be close to Al13Fe4 (Al: 65.4, Fe: 32.8, O: 1.8, all wt%) stoichiometry. This was also consistent with X-ray diffraction pattern (Fig. 5); dominant Al, and minor Al13Fe4 and Al2O3 peaks were detected. Relatively low intensity peaks of Al13Fe4 and Al2O3 confirms the occurrence of in-situ reaction between Fe2O3 particles and Al matrix.

The diffraction peaks corresponding to Fe3O4 established that Al–Fe2O3 reaction was not completed after four passes of FSP. In addition, two low-intensity-peaks in X-ray diffraction were found to be consistent with Fe3O4 crystal structure, which was expectable as an intermediate product in thermite reaction.

Fig. 6 shows the magnified image of Al/(Al13Fe4 + Al2O3) hybrid composite along with the elemental mapping analyses, which specified the particles with pale gray contrast are Al2O3 (this was previously indicated by X-ray diffraction pattern). In general, the size of Al2O3 nanoparticles was below 100 nm.

The microstructure of the hybrid composite specimen was further characterized by TEM (Fig. 7). Similar to the SEM results, various fine particles were found to be uniformly distributed in aluminum matrix. Typical aluminum grain size was ~2 μm. Fig. 7b shows an Al-diffraction pattern and dark field imaging using 200 reflection revealing the related aluminum grain.

Particles with elliptical (Fig. 8a) and irregular (Fig. 8b) shapes were detected in the fabricated composite. The elliptical particles were identified as Al13Fe4, with a typical size of ~100 nm (Fig. 8a). EDS analysis and X-ray diffraction pattern were found to be consistent with Al13Fe4 intermetallic. In addition, irregular floc-shaped particles were found to be α-Al2O3 and Fe3O4 (Fig. 8b) using selected area diffraction pattern (Fig. 8c). During FSP, Fe2O3 particles were fragmented and dispersed in aluminum matrix by the stirring action of the rotating tool; this encouraged the reaction between Al and Fe2O3 particles that resulted in the formation of Al2O3 and Al13Fe4 products.

The aluminum matrix grains were studied further using EBSD. Fig. 9 shows EBSD maps of different samples. Grains of the base alloy were elongated with a high amount of LAGBs (Fig. 9a and Table 2). In the case of the sample without powder addition, refined grains were observed (Fig. 9b). In fact, elongated grains of the base alloy changed to equiaxed ones with a mean grain size of ~8 μm. After processing with Fe2O3 particles, a finer grain structure was attained (Fig. 9c); the mean grain size was ~3 μm. These results support that particles produced by the reaction of Al and Fe2O3 had extra effect on reducing matrix grain size. FSP of both samples (with and without Fe2O3) resulted in increasing the fraction of HAGBs.

During FSP of the rolled alloy, there is a competition between grain refinement and recovery of the previous cold worked microstructure. Grain refinement is most likely done via modification of fine sub-grains structure on the bases of dislocations re-arrangements. Continuous dynamic recovery of aluminum involves progression and accumulation of dislocations at LAGBs, which leads to the transformation of LAGBs into HAGBs [19,20]. As compared to the sample without powder addition, the fabricated composite contained a higher portion of HAGBs. The dark lines in these maps represent HAGBs (>15° misorientation).
Fig. 4. (a) SEM micrograph and EDS X-ray maps of the fabricated composite using Al-K$_\alpha$, O-K$_\alpha$, and Fe-K$_\alpha$ radiations exhibiting elemental partitioning of A, B, C and D-type particles in Al matrix, (b) quantitative point analyses of A and (c) B particles.

Fig. 5. X-ray diffraction pattern of the fabricated Al/(Al$_{13}$Fe$_4$ + Al$_2$O$_3$) hybrid composite by FSP with Fe$_2$O$_3$. 
3.2. Mechanism of Al-Fe₂O₃ Reaction During FSP

The reaction between Al and Fe₂O₃ can be divided into several steps. Obviously, the formation of Fe₃O₄ indicated that a deoxidation reaction of Fe₂O₃ occurred under FSP (i.e. decomposition into Fe₃O₄ and O₂). Meanwhile, Al combines with oxygen and tends to transform to thermodynamically stable α-Al₂O₃. However, further progression of the reaction needs high temperatures, though intermediate and non-stable alumina such as κ-Al₂O₃ (as a common metastable Al₂O₃ polymorph) or even κ'-Al₂O₃ (as an unstable intermediate phase) are most likely to be formed [4,14]. In addition, a reaction between Fe₃O₄ and Al may lead to the formation of FeAl₂O₄ phase, which can be regarded as a transition phase under the non-equilibrated reaction [21]. This phase is often synthesized under high-temperature conditions [22,23] and stabilized in a controlled atmosphere with very low partial pressure of oxygen [24,25], the condition that only exists in closed systems. Moreover, FeAl₂O₄ phase can be reduced to Fe and Al₂O₃ by Al phase as reaction advances. Thus, these reactions are to be considered:

\[
\begin{align*}
3\text{Fe}_2\text{O}_3 & \rightarrow 2\text{Fe}_3\text{O}_4 + 1/2 \text{O}_2 \\
2\text{Al} + 3/2 \text{O}_2 & \rightarrow \text{Al}_2\text{O}_3 \\
\text{Fe}_3\text{O}_4 + 2\text{Al} & = \text{FeAl}_2\text{O}_4 + 2\text{Fe} \\
1/2 \text{FeAl}_2\text{O}_4 + 1/3 \text{Al} & = 1/2 \text{Fe} + 2/3 \text{Al}_2\text{O}_3
\end{align*}
\]

Fe₃O₄ particles of reaction (2) were uniformly distributed and surrounded by Al matrix due to complex material flow associated with FSP. This complex flow and severe plastic deformation enhanced

Fig. 6. (a) SEM micrograph and EDS X-ray (b) Al-Kα, (c) Fe-Kα, and (d) O-Kα maps of Al/(Al₁₃Fe₄ + Al₂O₃) hybrid composite specimen.

Fig. 7. (a) TEM bright field micrograph of the composite specimen (b) TEM dark field micrograph using 200 reflection of the presented Al diffraction pattern showing an Al grain.
the progression of reaction (3). In this case, many Al₂O₃ particles would nucleate and grow on Al/Fe₃O₄ interfaces along the special crystal orientation of the reactants (Fig. 10). In the subsequent FSP passes, most of Al₂O₃ particles would become separated from unreacted Fe₃O₄ and redistributed in the matrix. The existence of some intermediate Fe₃O₄ phases suggests that reaction (1) could not proceed completely during FSP, which made the volume fractions of Al₃Fe (very similar to Al₁₃Fe₄) and α-Al₂O₃ substantially lower than the calculated ones.

According to reactions (4) and (5), some free Fe atoms will be formed. The main intermetallic compound formed in Al–Fe system is Al₅Fe₂ by solid state reaction, [26]. There are several studies on microstructural analysis of interface layer when molten aluminum comes in contact with solid iron [27,28]. Recently, selective laser melting has been successfully applied to produce in-situ novel aluminum matrix composites from powder mixtures of Al and Fe₂O₃ [16]; Al₁₃Fe₄ was found as the main Al–Fe intermetallic especially in low concentration of Fe₂O₃. In addition, Lee et al. [29] used plasma synthesis method to fabricate in-situ Al–Fe composites. They suggested that the first phase nucleated on the interfacial layer of Al/Fe was Al₁₃Fe₄ (very similar to Al₅Fe₂) and due to the reaction between Al₁₃Fe₄ and Fe, Al₅Fe₂ phase formed and grew inward. The absence of Al₅Fe₂ in our FSP experiments might be due to short time of the method. Also, the

![Figure 8: TEM images showing (a) typical Al₁₃Fe₄ particle with elliptical shape and (b) irregular floc-shaped particles of the hybrid composite specimen consisting of α-Al₂O₃ and Fe₃O₄ species, and (c) electron diffraction patterns of b: irregular floc-shaped particles exhibiting a cluster-type morphology.](image1)

![Figure 9: EBSD images showing the matrix grain structure of (a) AA1050 base alloy and SZ of the work pieces processed (b) without and (c) with Fe₂O₃ addition (composite sample).](image2)
peak temperature is relatively lower than those of the other in-situ processing techniques [30]. In FSP, the heat generated by the rotating and advancing tool can initiate exothermic reactions. The heat of formation for Al$_2$Fe is ~28.1 kJ/g-atom (at 1173 K) and the heat of fusion of Al at 933 K is ~10.8 kJ/g-atom [31]. Thus, the heat release due to the exothermic reaction may cause eutectic melting of Al and Al$_{13}$Fe$_4$. The eutectic melting combined with the large plastic strain induced by the rotating tool may cause fragmentation of Al$_{13}$Fe$_4$ compound, which is then rapidly dispersed in the aluminum matrix. Because of the heat sink effect of the substrate, aluminum melt containing Fe is solidified rapidly. The time that material is affected by the rotating pin in FSP can be considered as the processing time. Based upon the pin diameter and tool traverse speed, the processing time was estimated to be <20 s. Because of the rapid cooling and vigorous stirring in FSP, fine Al$_{13}$Fe$_4$ particles can be formed during eutectic solidification. In addition, the solubility of iron in aluminum at solid state is very low (i.e., max. 0.05% at 650 °C [32]) and therefore, a supersaturated solute of Fe in Al matrix can also occur during rapid cooling, and fine Al$_{13}$Fe$_4$ particles would precipitate in the following FSP passes. It is suggested that nano-sized Al$_{13}$Fe$_4$ particles with elliptical shape, shown in Fig. 9, could form by either eutectic solidification or solid state precipitation in FSP. The time that material is subjected to thermo-mechanical action is very short in FSP. Thus, the presence of local melting at Al/Fe interface may be the key factor for the rapid progress of reaction. In addition, the large plastic strain imposed in FSP can effectively remove Al$_{13}$Fe$_4$ particles such that direct contact between Al and Fe can be maintained, and consequently, the reaction can proceed rapidly at the interface. Al$_{13}$Fe$_4$ particles could act as active nuclei for Al grains during solidification. In fact, since Al–Fe intermetallic compounds are very brittle, it is more likely that these particles are intermetallic compounds and fragmented due to the stirring action of the FSP tool. It seems that FSP can break intermetallic compounds so that the particles with sub-micron sizes are formed at some regions. It appears that these particles may be responsible for the formation of regions with very fine grained structure considering the pinning effect of sub-micron particles on grain boundaries of newly recrystallized grains during FSP [33,34]. Additionally, the presence of fragmented Al–Fe IMCs can result in the formation of very fine grained structure at the mentioned regions via particle stimulated nucleation mechanism [35].

3.3. Mechanical Properties

Fig. 11 shows the micro-hardness profiles of the central cross-sectional zones of the FSPed specimens (measurements were done on the dashed line). For comparison, micro-hardness measurement of the base AA1050 was also carried out. A slight increase in the hardness of base metal after FSP was attained. But marked hardness enhancement was resulted by the addition of Fe$_2$O$_3$ particles. Results show that grain refinement has limited effect on micro-hardness improvement of AA1050 alloy. Whereas, significant increase was obtained in the SZ with Fe$_2$O$_3$ powder owing to the occurrence of reactive reaction and its hard ceramic and intermetallic products; α-Al$_2$O$_3$ and Al$_{13}$Fe$_4$. These are very fine, hard and stable with good interfacial bonding, reinforcing the matrix. In addition, the relatively elliptical morphology of particles reduces the stress concentration associated with corners, which can better assist hardening of aluminum.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LAGBs%</th>
<th>HAGBs%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base AA1050</td>
<td>89</td>
<td>11</td>
</tr>
<tr>
<td>Without Fe$_2$O$_3$ addition sample</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>With Fe$_2$O$_3$ addition (composite sample)</td>
<td>37</td>
<td>63</td>
</tr>
</tbody>
</table>

The tensile stress–strain curves of the as-rolled AA1050 base alloy, fabricated hybrid composite and FSPed AA1050 alloy are shown in Fig. 12; the hybrid composite has an ultimate strength ~171 MPa, and a failure strain ~0.25. The ultimate tensile strength of composite specimen is much higher than those of as-rolled base and FSPed AA1050 alloy (~97 MPa). The major contributions to the high strength of the hybrid composite are considered to be Orowan strengthening caused by fine and uniform dispersion of nano-size particles (Al$_2$O$_3$ and Al$_{13}$Fe$_4$) and ultrafine-grained structure of the aluminum matrix. In addition, the ultrafine-grained structure of aluminum matrix is a result of fine dispersion of nano-particles via the Zener pinning effect [36]; dislocations were pinned by intergranular fine particles in the hybrid composite (Fig. 12b). It is interesting that the hybrid composite showed better ductility than AA1050 base alloy. This is believed to be attributed to improvement of its microstructure [37]. In addition, the FSPed AA1050 alloy showed a high engineering strain on fracture. Near result was also reported earlier by Ke et al. [38] on FSP of 1060Al alloy. It is documented that few inclusions are in the microstructure of AA1050 alloy [39]. This associated with grain refinement by FSP increased elongation on tensile fracture. However, although further grain refinement resulted in the hybrid nano-composite, elongation decreased due to the presence of hard reinforcements.

![Fig. 10. Schematic of formation mechanism of Al$_{13}$Fe$_4$.](image)

![Fig. 11. Micro-hardness profiles across the SZ of AA1050 base alloy and work pieces processed with and without Fe$_2$O$_3$.](image)
4. Conclusions

In this study, in-situ Al/(Al13Fe4 + Al2O3) hybrid composite was fabricated from an Al–Fe2O3 system by friction stir processing. The most important results are summarized as follows:

1. Exothermic reaction of Al–Fe2O3 system was initiated and progressed due to the combination of high temperature and large plastic strain associated with FSP. However, the existence of intermediate phases suggests that the reaction was not completed during the short time of FSP.

2. The reinforcing phases were identified as Al13Fe4 intermetallic and α-Al2O3. The fabricated hybrid composite showed a fine grained Al matrix with mean grain size of ~3 μm.

3. The Al matrix microstructure of the FSPed work piece without Fe2O3, consisted of a large amount of HAGBs with high misorientation angles. As compared to the sample without powder addition, the composite contained a higher portion of HAGBs.

4. The in-situ formation and dispersion of nanoparticles in the aluminum matrix together with grain refinement significantly increased the strength of the fabricated Al/(Al13Fe4 + Al2O3) hybrid composite.

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