Enhanced Mechanical and Erosion-Corrosion Properties of Al/Nano Al$_2$O$_3$ Composite by ECAP

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Abstract— Aluminum composites are widely used in several applications due to light weight, outstanding strength, erosion corrosion resistance, and good formability. With the aim to study the effect of the severe plastic deformation (SPD) on the mechanical properties and erosion corrosion resistance of aluminum composites; in the current study equal channel angular pressing (ECAP) was applied for consolidation of aluminum powder (50 μm) with varying concentrations of aluminum oxide (Al$_2$O$_3$) Nano-powders (40 nm). The homogeneity of the nano particles distribution due to ECAP was examined and the variations of the mechanical properties were investigated. The fracture surface and erosion corrosion resistance of the composite was also investigated. The results had showed that the ECAP process enhanced the distribution of reinforcement material, tensile strength, Vickers hardness value, and erosion corrosion properties of Al/Nano Al$_2$O$_3$ composite.

Index Term— Aluminum composite, ECAP, Erosion corrosion, Powder metallurgy

1. INTRODUCTION
Metal matrix composites (MMCs) and Metal matrix Nano composites (MMNCs) are very significance for many applications such as aerospace, military, and automotive industries. MMNCs are manufactured using several techniques [1]. These techniques could be classified as (a) liquid-state processes: stir casting, squeeze casting, ultrasonic-assisted casting, vacuum infiltration , pressure less infiltration, and dispersion methods, (b) solid state processes: powder metallurgy (PM) techniques with variations in the processing steps e.g. hot iso-static pressing, cold iso-static pressing, hot die pressing, dynamic compaction , and (c) liquid-solid processing: compo-casting, semisolid forming. The restrictions of the first and third groups come from complications in mixing the two phases, difficult determination of infiltration critical temperature, and wettability at the interface of matrix-reinforcement[1][2][3]. Aluminum MMNCs are considered as advanced materials due to its high strength, light weight, low coefficient of thermal expansion and good wear resistance [4]. Reinforcing the aluminum matrix with stronger reinforcements like aluminium oxides and silicon carbides provides several properties of the matrix and ceramic reinforcement components [5]. Normaly, consolidation processes are capable of consolidating nano powders by heat and pressure. However, they usually result in grain growth, which leads to loss of the nanostructure [6]. The powders can be consolidated at room temperature by using severe plastic deformation (SPD) techniques. The principle of SPD is based on increasing dislocations via severe deformation of the material [7]. SPD can be achieved through different techniques, one of which is equal channel angular pressing (ECAP) [8]. In the ECAP process, the material passes through two intersecting channels that have equal diameters under forced shear deformation. The ECAP process can be performed multiple times in order to achieve the desired properties. Compared to other conventional metal forming processes the ECAP is capable to attain a high strain without changes of samples dimensions [8]. Sedivy et al. applied ECAP to pure copper for characterization of the material [9]. However, more studies are still required to investigate the effects of ECAP on other metallic materials. The reported performance enhancement of ultrafine grained and nanostructured materials proposes that there may also be an improvement in their erosion corrosion behavior. Furthermore, the enormous amount of deformation ECAP can be useful in producing MMCs with uniform distribution. It was proposed that the fracture is accelerated by high local stresses leading to fracture initiation in particle clusters [10][11]. Christian et al [12] found that the particle clustering resulted in lower composite flow stress, in comparison to a composite with homogeneous particle distribution. Based on the literature review, it seems important to use further techniques for better particle distribution in MMCs, which may cause better utilization of materials. The current study emphasizes on the using of ECAP method for better distribution of alumina (Al$_2$O$_3$) nano particles reinforcement in the aluminum matrix and comparing with the conventional materials. Moreover, the effect of ECAP on mechanical properties and erosion corrosion resistance of the new
composite was investigated.

2. EXPERIMENTAL WORK

In this work, purity aluminum powders with an average particle size of about 50 μm were used as matrix material. Alumina (Al₂O₃) reinforcement powder with purity of 99.9% and an average size of 40 nm was utilized to make the MNMC. Scanning electron microscopy (SEM) of as-received aluminum and Al₂O₃ particles are presented in Fig. 1.

The powder mixtures were wet in ethanol slurry in a container with steel balls (diameter of 6 mm and a rotational speed of 450 rpm) for about 8 hours. After the ethanol removal the powder mixture was dried in an oven at 180°C for 60 min. Thin walled copper tubes were prepared as casing and filled with aluminum composite powders. The powder was added gradually by a funnel and carefully pressed by hand and then new powder added to fill the copper tube completely. Equal channel angular pressing (ECAP) was applied at 200°C on the specimens for four passes with route ‘Bc’. With route ‘Bc’ the specimen is rotated 90° clockwise after each pass. The dimensions of samples before and after ECAP passes are shown in Fig. 2. The inner and outer angles of the ECAP die were φ = 90°, ψ = 20°, and the cross section was d = 15 mm as displayed in Fig. 3.

Archimedes’ principle was used according to specifications for density measurements for porous materials to determine the densities of the samples. Relative densities are based on the theoretical density and measured values. Table 1 shows the relative density for samples before and after 4 ECAP passes.
Table I

<table>
<thead>
<tr>
<th>Relative density (%)</th>
<th>As received material</th>
<th>Al/10vol. %Al₂O₃</th>
<th>Al/15vol. %Al₂O₃</th>
</tr>
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<tbody>
<tr>
<td>Before ECAP</td>
<td>73.5</td>
<td>48.8</td>
<td>45.7</td>
</tr>
<tr>
<td>After ECAP</td>
<td>99.2</td>
<td>98.6</td>
<td>94.4</td>
</tr>
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In order to conduct hardness test, samples with 15 mm diameter and thickness of 5 mm were cut from the ECAPed specimens. These samples were cleaned and polished. Vickers hardness machine (model Zoiwek-250) was used for measuring the hardness by applying the load for 10 s. Each hardness value was determined by using three separate samples in the same processed condition and taking the average of five readings on each of them. In addition, the microstructure of all the samples were analyzed using scanning electron microscopy. The erosion-corrosion (E-C) tests were conducted according to ASTM G31-72 and G119 standards in order to investigate the effect of ECAP on wear resistance of the material [13] [14] in a slurry pot tester that developed by the authors of current study for this purpose. The developed slurry pot consists of a cylindrical stainless steel pot. Its dimensions are 300 mm diameter and 300 mm height to handle large slurry volume. A disc has a diameter of 200 mm and thickness of 25 mm was bolted to a shaft. The whole assembly was attached to the spindle of a 1.5 KW drilling machine through a rigid coupling. The drilling machine has a maximum speed of 1650 rpm. In order to have different linear speeds, the samples are mounted to the disc at different radial distances. The required linear speed can be calculated from the following equations:

\[ v = \omega r \]  
\[ \omega = 2\pi N \]  
\[ v = \frac{2\pi N r}{60} \]

Where, \( v \): linear velocity (m/s), \( \omega \): angular velocity (rad/s) and \( N \): Number of revolutions per minute (rpm), and \( r \): radius of rotation (mm). The sample holders could be revolved to allow the erodent medium impacting the sample surface at different desired angles. The slurry pot and details of the disc are shown in Fig. 4. A slurry solution of 3.5 wt. % sodium chloride (NaCl) and SiO₂ with average size of 250 – 400 μm was used in the tests. Before and after each E-C test the samples were whased by distilled water and cleaned by acetone. Then a precision digital balance with a resolution of 0.01 mg was utilized to weight the samples. Each test had been repeated three times, and the average weight loss was recorded. Then the weight loss per unit area was calculated.

Different approaches were used previously to improve reinforcement distribution in MMCs. Lewandowski et al. [15] examined the influence of particle size and distribution on the damage resulting in failure. The distribution uniformity of Al₂O₃ particle was studied by the quadrat method that considered the most effective technique for that purpose [16] [17]. With the quadrat method, the images were divided into a grid of square cells and the number of particles in each cell, \( N_q \), was calculated. A clustered distribution may be expected to produce empty quadrats, quadrats with a small number of particles, and quadrats with many particles. A random distribution would be anticipated to produce results somewhere in between these two extremes [18]. A simple rule used in this study is that the appropriate square quadrat size should be approximately twice the size of the mean area per particle [19]. Quadrat sides are counted to minimize the edge effects, the number of particles inside and in contact with the left and bottom of the specimen. The results from the quadrat analysis can be compared with theoretical distributions defined by statistical approaches. Random distributions of particles can be
expressed in mathematical terms if the particles are assumed to be with cross-sectional areas of zero (point). Mathematically, the random distribution of points follows the Poisson model, a regular distribution follows the binomial model, and a clustered 3 dimensional distribution follows the negative binomial model. SEM images were taken for polished section of 10 and 15 vol. % composites after the 1st and the 4th pass of ECAP. Each image was divided into 117 quadrats. The size of each quadrat was set to a = 0.9 μm, as the optimum quadrat size should be twice the size of the mean area per particle. The experimental particle number per quadrat distributions were compared to two theoretical distributions: (i) the Poisson distribution (equation 4), which should be valid for a homogeneous particle distribution (ii) The negative binomial distribution (equation 5), which corresponds to a clustered particle distribution [20].

\[ P(r) = \frac{\mu^r}{r!} \exp(-\mu) \]  \hspace{1cm} (4)

\[ P(r) = \frac{(k + r - 1)!}{(k - 1)!r!} \left( \frac{p}{1 + p} \right)^r \left( \frac{1}{1 + p} \right)^k \]  \hspace{1cm} (5)

In the above equations, P(r) is the probability, r is a variable (the number of particles per quadrat), μ the mean value of the number of particles per quadrat, k measures the degree of clustering associated with the process. As k approaches to zero, the distribution converges on an exceptionally clustered distribution. After dividing the images into 117 quadrats, the number of particles in each cell was counted and the number of total particles and the mean number of particles was determined. The Poisson distribution and the negative binomial distribution were determined for each image. The microstructures images expose that the Nq distribution varies with the degree of clustering. Indeed, increasing the size of Al₂O₃ clusters results in less symmetric Nq distribution. The degree of asymmetry of the distribution around the mean can be measured by its skewness, β, which is defined by.

\[ \beta = \frac{q}{(q-1)(q-2)} \sum \left( \frac{N_q - N_q^{\text{mean}}}{\sigma} \right)^3 \]  \hspace{1cm} (6)

Where q is the total number of quadrats, Nqi the number of Al₂O₃ particles in the ith quadrat (i = 1, 2… q), mean Nq the mean number of Al₂O₃ particles per quadrat and σ the standard deviation of the Nq distribution.

3. RESULTS AND DISCUSSION

The frequency graph of the number of Al₂O₃ particles per quadrat (Nq) for Al/10 vol% Al₂O₃ and Al/15 vol% Al₂O₃ composites after the 1st pass and 4th pass of ECAP are shown in Fig. 5 and Fig. 6, respectively. It is clear that the frequency of empty quadrats decreases with the increasing the number of ECAP passes. The graphs of the distribution for Al/10 vol% Al₂O₃ after the 1st pass of ECAP (Fig. 5a) follow the binomial distribution, but by increasing the number of ECAP passes the distribution converges to the Poisson distribution. Although four passes of ECAP is not sufficient for Al/15 vol% Al₂O₃ to fit the data to the Poisson distribution, the number of empty quadrats and the ones containing four particles decrease from 27 to 22 and 3 to 1, from the 1st pass to the 4th pass, respectively. This is an indication of better distribution of the reinforcement Al₂O₃ particles. It can be concluded that during ECAP, large Al₂O₃ particles break to some extent, principally for Al/15 vol% Al₂O₃ composite, and shear deformation moves some particles in the microstructure and leads to better distribution. However, this effect diminishes as the amount and the size of Al₂O₃ particles decreases. Because of this fact that small particles need a great active plastic flow, which is not achieved during ECAP process.
According to table II, the skewness does not change significantly for 10 vol. % composites where the amount of clustering is less. The skewness decreases from about 0.79 after the 1st pass to 0.58 after the 4th pass of ECAP for 15 vol. % composite. This is an indication of declustering of particles. However, the graph for Al/15 vol. % Al₂O₃ composites looks as if it follows the negative binomial distribution (Fig. 6a, b), indicating also a clustered particle distribution.

Table II

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Al/10 vol. % Al₂O₃</th>
<th>Al/15 vol. % Al₂O₃</th>
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<tbody>
<tr>
<td></td>
<td>Pass1</td>
<td>Pass2</td>
</tr>
<tr>
<td>σ</td>
<td>0.965</td>
<td>0.952</td>
</tr>
<tr>
<td>β</td>
<td>0.82</td>
<td>0.73</td>
</tr>
</tbody>
</table>

In order to interpret how much the Al₂O₃ particles assist in strengthening, image analysis with image tool software was carried out on the SEM micrographs of Al/15 vol% Al₂O₃ composite, and the frequency was displayed against Al₂O₃ particle size. Fig. 7a shows that about 26% of Al₂O₃ particles are below 300 nm after the 1st pass, whereas after the 4th pass of ECAP (Fig. 7b) 57% of Al₂O₃ particles lay in this category. This indicates more contribution of the nano Al₂O₃ particles in strengthening the material and confirms the decrease in skewness that enhances Al₂O₃ declustering with increasing the passes of ECAP.
Fig. 7. Frequency versus Al₂O₃ particle size for Al/15 vol% Al₂O₃ composite [20]
(a) after ECAP pass1 and (b) after ECAP pass2

Fig. 8 (a-c) presents the SEM images of the Al/15 vol% Al₂O₃ composite before ECAP, after the ECAP pass2, and pass4, respectively. Better distribution of Al₂O₃ particles (solid arrows) was achieved after four passes of ECAP in comparison to as received material. The microstructural examinations display that the Al₂O₃ particles break during the ECAP process and move to free particle zones simultaneously with the elimination of porosity by increasing the number of ECAP passes [20]. This is more clear in case of 15 vol.% Al₂O₃ composite due to higher agglomeration in comparison to 10 vol.% Al₂O₃ composite, which has less agglomeration. The increase in density is more significant for the ECAPed specimens than the as received ones. Therefore, the required loads increase if the final part size is to be sustained. For achieving the same total strain in ECAP with higher ratio of 20:1, SEM image of the as received sample and the one ECAPed for two passes are compared in Fig. 8. Better Al₂O₃ distribution and smaller clusters can be seen in figure 8c. This is a sign for the effectiveness of ECAP process in enhancing the reinforcement particles. The repetitive loading of the specimens when they undergo shear deformation at the intersection of the entry and exit ECAP die channels generates stress concentrations locally in the clusters. So, it is reasonable to show the required force for particle declustering during ECAP, which produces stress and accumulated strain. Fig. 9 shows the stress-strain curves for 15 vol. % Al₂O₃ composite after the 1st and 4th pass of ECAP, respectively.

Fig. 8. SEM images of the Al/15 vol. % Al₂O₃ composite
(a) as received extruded material, (b) after ECAP pass2, and (c) after ECAP pass4

It is clear that the stress increases by increasing the number of passes due to strain hardening of the material and the consolidated powder. According to the graph, the maximum required stress is nearly two times greater for the 4th pass than the 1st pass. Fig. 10 shows a significant increase in Vickers hardness of Al/vol.15%Al₂O₃ through all ECAP passes compared to Al/vol.10%Al₂O₃ and as received specimen. Literature shows that such results were obtained for other materials [18-20].
In order to investigate the distribution of Al₂O₃ particles, it is important to examine the fracture surface of Al/15 vol% Al₂O₃ composite after the 4th pass of ECAP and for as received composite. It is noticeable from Fig. 11 that the ECAP has a significant effect on Al₂O₃ distribution due to more homogeneity of particles. The fracture surface for the as received sample is not as homogeneous as the ECAPed one, which is an indication of random detachment of Al₂O₃ particles from the matrix and inadequate distribution of Al₂O₃ in the matrix material. The erosion corrosion (E-C) was investigated through the influence of experimental duration on the weight-loss of the specimens. The mean values of weight-loss were calculated by averaging three experimental data and represented. The standard deviations were represented by the error bars [21-23]. The time effect was studied for as received Al/Al₂O₃ composite as well as Al/vol.10% Al₂O₃ and Al/vol.15% Al₂O₃ composites at different ECAP passes. Fig. 12 and Fig. 13 show the variation of weight loss per unit area with ECAP passes at different testing durations for Al/vol.10% Al₂O₃ and Al/vol.15% Al₂O₃ respectively. The tests were performed at 300 hours, 500 hours, 750 hours and 1000 hours at constant conditions: a velocity of 3m/s, an impacting angle of 45°, and simulated sea water containing sand particles as an erodent material.

Fig. 9. Stress-Strain curve for 15 vol. % Al₂O₃ composite after the ECAP pass1 and ECAP pass4

Fig. 10. Hardness variation versus ECAP passes

Fig. 11. Fracture surface of the Al/15 vol. % Al₂O₃ composite, (a) as received extruded composite, (b) after the ECAP pass4
The results revealed that the time variation affects the E-C resistance of both Al/vol.10% Al₂O₃ and Al/vol.15% Al₂O₃ at different ECAP passes. Regarding Al/vol.10% Al₂O₃, the samples before ECAP experienced weight losses of 2x10⁻⁶ gm/mm², 4.2x10⁻⁶ gm/mm², 8.2x10⁻⁶ gm/mm² and 12.1x10⁻⁶ gm/mm² at durations of 300, 500, 750 and 1000 hours respectively. No significant difference in the weight loss could be observed for 300 hours and 500 hours while more difference was observed for the 1000 hours test (12.1 x10⁻⁶ gm/mm²). The reason for the improvement can be interpreted as follows: After first, second, third and the fourth passes of ECAP, the hardness increased gradually. After four ECAP passes the weight loss due to E-C decreased. With respect to Al/vol.15% Al₂O₃ the samples before ECAP showed weight losses of 0.7x10⁻⁶ gm/mm², 1.8x10⁻⁶ gm/mm², 2.4 x10⁻⁶ gm/mm² and 3.8 x10⁻⁶ gm/mm² at durations of 300, 500, 750 and 1000 hours respectively. The results showed no significant difference in the weight loss for 300 hours and 500 hours while more difference was observed for the 1000 hours test (12.1 x10⁻⁶ gm/mm²). With increasing the number of ECAP passes the weight loss decreases. This is an indication of the positive effect of ECAP on enhancing the E-C resistance of Al/vol.10% Al₂O₃ and Al/vol.15% Al₂O₃.

4 CONCLUSION

In this study the effect of particle reinforcement on properties of Al/Al₂O₃ composite was investigated by the quadrat method. ECAP process was applied on the composite powder. The results showed that the ECAPed samples after four ECAP passes have better distribution of particles, improved mechanical properties and in turn have more erosion corrosion resistance. Among the ECAPed samples, the variation in skewness is more significant for Al/15 vol. % Al₂O₃ composite than Al/10 vol. % Al₂O₃ composite. This is because of higher amount of Al₂O₃ agglomeration in Al/15vol. % Al₂O₃ composite, which causes fragmentation of Al₂O₃ particles from the surface of the clusters and their movement to particle-free zones. Increasing the number of ECAP passes leads to an increase in tensile strength by more than two times. Fracture surface showed that ECAP has a significant effect on Al₂O₃ distribution than as received material due to more homogeneity of Al₂O₃ particles in the matrix.

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