Strengthening analyses and mechanical assessment of Ti/Al₂O₃ nano-composites produced by friction stir processing

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The present work investigates strengthening mechanisms and mechanical assessment of Ti/Al₂O₃ nano-composites produced by friction stir processing of commercially pure titanium using nano-sized Al₂O₃ with different volume fractions and particle sizes. Microstructural analyses were conducted to characterize the grain size of matrix, size and dispersion of reinforcing particles. The mean grain size of the composites ranged from ~0.7 to 1.1 μm that is much lower than 28 μm of the as-received material. Reduction of grain size was found to be in agreement with Rios approach (based on energy dissipated during the motion of an interface through particle dispersion), and showed deviation from Zener pinning model. Scanning and transmission electron microscopies revealed a near uniform dispersion of Al₂O₃ nano-particles, with only a small fraction of widely spaced clusters. The maximum compression yield strength of the fabricated nano-composite (Ti/3.9%vol of 20 nm-Al₂O₃) was found to be ~494 MPa that is ~1.5 times higher than that of the as-received material. Strengthening analyses based on grain refining (Hall–Petch approach), load transfer from matrix to reinforcements, Orowan looping, and enhanced dislocation density due to thermal mismatch effects were carried out considering Al₂O₃ reinforcement with different volume fractions and sizes. However, Hall–Petch approach was found to be the dominant mechanism for the enhancement of yield strength.

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1. Introduction

Metal matrix composites reinforced by ceramic particles have been investigated widely in recent years due to their excellent properties such as strength, hardness and stiffness. In this context, titanium is of particular interest as a matrix because of its desirable mechanical, physical and chemical properties. Different types of ceramic particles such as TiC [1], Al₂O₃ [2–3], and SiC [4] have been used to reinforce titanium matrices. Al₂O₃ offers a low cost material to achieve high strength, resistance to thermal shocks, great chemical stability and low density. Furthermore, its coefficient of thermal expansion (CTE) is relatively near to that of titanium which is a considerable parameter in producing titanium-based composites reinforced by alumina particles [5–6]. Most applications for titanium based composites involve the automotive and aeronautical and biomedical industries, while a time-of-flight mass spectrometer has also recently been demonstrated to use Ti/Al₂O₃ composites [5–7].

The high production cost is one of the main problems in most conventional metal matrix composite manufacturing processes. This mainly results from the long processing time, high electric power consumption and specialized equipment required [8]. In recent years, friction stir processing (FSP) has been used as an effective process in the production of different metal matrix composites [9–13]. Low processing temperature makes it possible to produce composites in solid state condition, which is particularly important when attempting to fabricate nano-composite reinforced particles since these are more prone to reaction with the matrix at elevated temperatures. In addition, porosity at matrix/particle as a result of difference in CTE can be limited due to lower processing temperature.

Since FSP method maintains the material in the solid phase and imposes severe plastic deformation during processing, this helps to avoid many of the difficulties related to processing of composites in the liquid phase, such as poor wetting and tendency of particles to form clusters. These issues become more important when using nano-sized particles instead of micron-sized reinforcements, since the surface area to volume ratio is drastically higher.

In the present study, titanium based nano-composites are produced employing FSP and utilizing different sizes of Al₂O₃ nano-particles. The strengthening mechanisms and the effect of
some parameters such as the size, volume fraction and distribution of particles on the mechanical properties of the fabricated composites were investigated. Finally, a model was introduced for predicting the yield strength of the nano-composites based on the associated strengthening mechanisms, volume fraction and particle size of reinforcements.

2. Materials and methods

Commercially pure Ti (CP-Ti) grade 2 plates with a thickness of 5 mm and Al₂O₃ (99.9% purity) powders with nominal particle sizes of 20 and 80 nm were used as the as-received materials. CP-Ti plates and Al₂O₃ powders were supplied by IMI-Birmingham (UK) and Nano-structured & Amorphous Materials Inc. (U.S.A.), respectively. 80 nm-Al₂O₃ powder had an alpha crystal structure while 20 nm-Al₂O₃ powder had a dominant alpha and minor gamma crystal structure. Volume fraction of gamma phase is estimated to be ~5% to 10%. FSP was carried out using a modified conventional vertical milling machine, equipped with an argon gas shrouding system. In order to perform FSP, a composite-type tool was made with a shoulder of hardened H-13 tool steel and pin of tungsten carbide. Shoulder and pin diameters were 15 and 5 mm, respectively. Pin length was 3.5 mm. CP-Ti work pieces were prepared with a length and width of 100 and 50 mm, respectively. A groove was made in a straight line along the middle length of each work piece. A fixed groove depth of 3 mm was applied. However, the groove widths were various according to Table 1. Nano-sized alumina particles were inserted into the groove. Before FSP, each work piece was fixed and held tightly by a fixture. In order to plasticize the substrate surface layer, the composite-type tool was set perpendicular to the fixed substrate with no tilt angle. A conventional vertical milling machine was employed for FSP tests. The tool was rotated by the machine in contact with work piece surface and advanced in a line along the groove. FSP experiments were carried out on CP-Ti work pieces with and without alumina powder using a fixed rotating and travel speed of 500 rpm and 150 mm/min using an argon gas shrouding system, respectively [4]. In order to investigate the influence of reinforcements on composites properties and to study the strengthening mechanisms, all the samples were divided to 3 different groups. The first group contains only CP-Ti which underwent FSP (without addition of Al₂O₃), the second group corresponds to CP-Ti with the addition of 80 nm reinforcing particles, and the last group involved CP-Ti reinforced with 20 nm Al₂O₃ powders. In the case of composite samples (groups 2 and 3) the width of the groove containing the initial powder ranged from 0.8 to 1.6 mm to obtain different volume fractions of reinforcements. Details of parameters selected for each sample are listed in Table 1.

Microstructural characterization studies were conducted on transverse cross-section planes of both the Ti plate base material and composite samples after FSP. The samples were ground, polished, and etched by a mixture of 10 ml HF, 5 ml HNO₃, and 85 ml diluted water solution. An Olympus metallographic microscope was used to investigate morphological characteristics of grains. The mean grain size was determined using linear intercept method. A Hitachi S4100 field emission scanning electron microscope (FE-SEM) was employed to analyze the reinforcement distribution. After analyzing a series of FE-SEM images for each sample, the size distribution of the Al₂O₃ particles was determined; area fractions of reinforcements obtained using Clemex image analyzing software [14] are reported as volume fraction of reinforcements. In addition, transmission electron microscopy (TEM) studies were performed to investigate more details of microstructure and also interfacial integrity between matrix and reinforcements. For TEM studies, thin foils parallel to a longitudinal section were prepared by ion milling, then observed in a CM12 microscope (by Phillips Ltd.) operated at 120 kV. Vickers hardness measurements have been carried out through the cross section of the stir zone on a horizontal line along the middle height of stir zones using a 300 g load and a 15 s holding time. Yield strength of specimens was measured by employing compression test. For this purpose, three cylindrical specimens of 3 mm diameter and 4.5 mm in height were cut from the center of the stir zones of each specimen by electrical discharge machining so that the compression axis was parallel to the direction of FSP tool traveling. The compression tests were conducted in room temperature with a strain rate of \(10^{-2} \text{ s}^{-1}\).

3. Results

Since the microstructure and/or the particle distribution would be difficult to reach a completely homogeneous state along the locations within stir zones [4], all the following results are taken from central regions of stir zones. Optical micrographs of Fig. 1 show the microstructure of the as-received CP-Ti, and central regions of stir zones of Ti–4p and Ti–80n–0.8 samples. The as-received CP-Ti exhibits a typical Ti plate grain structure with equiaxed primary \(\alpha\) grains and deformation twins, as shown in Fig. 1a. The mean grain size of this microstructure was found to be ~28 \(\mu\text{m}\). Fig. 1b and c shows the microstructures of the stir zone in the Ti–4p and Ti–80n–0.8 samples, respectively. Both microstructures contain fine, equiaxed and dynamically recrystallized grains which are significantly smaller than that of the as-received CP-Ti.

The grain size distribution of FSP treated CP-Ti, and composite samples reinforced with 80 nm and 20 nm Al₂O₃ particles were statistically measured; the corresponding histograms are shown in Fig. 2. Each histogram is the result of studying at least three fields taken from the central regions within the stir zones of each specimen. Histograms obtained for CP-Ti samples without reinforcements after one, three, and four FSP passes can be seen in Fig. 2a through c, respectively. The mean grain size of the samples after one FSP pass is ~4.4 ± 2.1 \(\mu\text{m}\) and this is further reduced

<table>
<thead>
<tr>
<th>Group no.</th>
<th>Sample name</th>
<th>Reinforcement</th>
<th>Number of processing passes</th>
<th>Groove width</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti–1P</td>
<td>N.A</td>
<td>1</td>
<td>N.A</td>
</tr>
<tr>
<td></td>
<td>Ti–3P</td>
<td>N.A</td>
<td>3</td>
<td>N.A</td>
</tr>
<tr>
<td></td>
<td>Ti–4P</td>
<td>N.A</td>
<td>4</td>
<td>N.A</td>
</tr>
<tr>
<td>2</td>
<td>Ti–80n–0.8</td>
<td>80 nm Al₂O₃</td>
<td>4</td>
<td>0.8 mm</td>
</tr>
<tr>
<td></td>
<td>Ti–80n–1.2</td>
<td>80 nm Al₂O₃</td>
<td>4</td>
<td>1.2 mm</td>
</tr>
<tr>
<td></td>
<td>Ti–80n–1.6</td>
<td>80 nm Al₂O₃</td>
<td>4</td>
<td>1.6 mm</td>
</tr>
<tr>
<td>3</td>
<td>Ti–20n–0.8</td>
<td>20 nm Al₂O₃</td>
<td>4</td>
<td>0.8 mm</td>
</tr>
<tr>
<td></td>
<td>Ti–20n–1.2</td>
<td>20 nm Al₂O₃</td>
<td>4</td>
<td>1.2 mm</td>
</tr>
<tr>
<td></td>
<td>Ti–20n–1.6</td>
<td>20 nm Al₂O₃</td>
<td>4</td>
<td>1.6 mm</td>
</tr>
</tbody>
</table>
to \( \sim 2.7 \pm 1.2 \mu m \) after three passes in sample Ti–3P, then to \( \sim 2.6 \pm 1.2 \mu m \) after four passes in sample Ti–4P. An increase in the number of FSP passes appears to become ineffective beyond 3 passes in the CP-Ti material. In addition, these histograms appear to suggest that a log-normal distribution in grain size is maintained after each FSP procedure in the CP-Ti material. Grain size histograms of samples Ti–80n–0.8, Ti–80n–1.2 and Ti–80n–1.6 are shown in Fig. 2d to f, and indicate a reduction in grain size with increasing volume fraction of particles (resulting from the increasing groove width from 0.8 to 1.6 mm). This trend is also apparent in samples containing 20 nm Al\(_2\)O\(_3\) particles (see Fig. 2g to i). The reduction in grain size values in the composite samples (Fig. 2d through 2i) compared to the unreinforced Ti–4P sample (Fig. 2c) clearly demonstrates that a significant grain refinement is achieved through the addition of nano-particles. Also, it should be pointed out that, smaller particles (20 nm) played a more effective role in decreasing matrix grain size. These histograms demonstrate that ultra-fine grained (< 1 \( \mu m \)) matrix grains can be readily achieved in the composite samples using both size ranges of nano-particles.

Fig. 3 contains FE-SEM images showing the distribution of the reinforcing particles in the titanium matrix for samples Ti–80n–1.2 and Ti–20n–1.2. It is clear that the particle distribution in the matrix is not completely uniform.

In both the images, distribution of particles varies from region to region. Some particles clustered and formed larger particles, meanwhile in many areas the particles are separated and more finely dispersed. In other words, in Fig. 3a and b, some particles have formed clusters which are larger than initial particles and others are separated as in the primary particles. After analyzing a series of FE-SEM images for each sample, histograms depicting the size distribution of the Al\(_2\)O\(_3\) particles are plotted in Fig. 4. In each histogram, the calculated values for mean particle size and standard deviation are listed.

For both groups of composites containing 20 and 80 nm particles, it is clear that the mean cluster size is greater than nominal particle sizes, although single and completely separated particles can be identified in the micrographs, as well. The average cluster size slightly increases with increasing volume fraction of particles for both size ranges of Al\(_2\)O\(_3\) particles used. In other words, lower volume fractions lead to smaller mean cluster sizes (which are closer to initial particle sizes). In addition, increasing the volume fraction of reinforcements leads to a higher number of clusters which shifts the distribution histograms toward larger sizes. The minimum volume fraction is \( \sim 1.8\% \) for sample Ti–80n–0.8 and the highest fraction is \( \sim 5.7\% \) for the Ti–20n–1.6 sample. As previously expected, a wider initial groove containing the powders resulted in a higher volume fraction of particles. As an example, for composites reinforced by 20 nm particles, the volume fraction increased from \( \sim 2.2\% \) to \( \sim 5.7\% \) with increasing groove width from 0.8 to 1.6 mm.

Hardness profiles across the transverse plane of the tool movement for FSP samples of CP-Ti and both nano-composites are illustrated in Fig. 5. In the CP-Ti, it is revealed that performing FSP has only caused a marginal enhancement in hardness where the average hardness of the stir zones is \( \sim 178 \) HV, \( 190 \) HV and \( 193 \) HV after one, three and four FSP passes respectively, as compared to \( \sim 172 \) HV in the as-received CP-Ti. However, the hardness profiles for the composites shown in Fig. 5b and c show a significant improvement in hardness compared to CP-Ti. It should be noted that the composite containing 20 nm particles had higher average hardness values compared to samples containing 80 nm particles, and the hardness values increased with volume fraction (resulting from wider groove sizes increasing from 0.8 to 1.6 mm).

Fig. 1. Optical micrograph showing stir zone microstructure: (a) the as-received CP-Ti; (b) Ti–4P; and (c) Ti–80n–0.8 samples.
Furthermore, samples containing a lower volume fraction of Al₂O₃ have a more uniform distribution of hardness across the processed region, and less scatter in hardness results can be noted when a 0.8 mm groove size was used during fabrication.

Fig. 6 compares the average hardness of composites against volume fraction for both the 20 and 80 nm particles. It can be noted that for both the composites an increase in volume fraction of reinforcements leads to an enhancement in hardness, while higher volume fractions could also be achieved using 20 nm particles.

Typical stress–strain curves for the CP-Ti after FSP and nano-composites reinforced with particles of 80 nm and 20 nm are shown in Fig. 7. In order to compare the compression behavior of the processed samples with that of the as-received Ti, the typical stress–strain curve of the as-received Ti is also plotted in Fig. 7a through 7c. From Fig. 7a, it can be concluded that, performing FSP without introducing reinforcements has not had a considerable effect on deformation behavior of Ti, and the yield strength of the FSPed samples is only slightly higher than that of the as-received CP-Ti. The 0.2% offset yield strength of the as-received CP-Ti sheet was found to be $\sim 307$ MPa, while the yield strength values of the unreinforced Ti increase with number of FSP passes, reaching a maximum value of $\sim 351$ MPa after 4 passes.

However, in the case of reinforced samples (Fig. 7b and c), the yield strength is considerably enhanced compared to the as-received Ti sheet. A maximum yield strength value of $\sim 494$ MPa was achieved for the sample Ti–20n–1.2, which is $\sim 187$ MPa (i.e. 61%) greater than that of the as-received CP-Ti. It is also clear in Fig. 7 that the work hardening increment of both as-received Ti and unreinforced samples is higher than that of the composite samples.

4. Discussion

4.1. Microstructure

Significant grain refinement occurs in the CP-Ti due to performing FSP even without introducing reinforcing particles as shown in Figs. 1 and 2. This has been reported in previous studies regarding FSP or friction stir welding (FSW) of CP-Ti [5,15–19]. Lee et al. [16] investigated the microstructure following FSW of pure Ti. They explained that the microstructure of stir zone contains a large number of deformation twins, randomly oriented inside the recrystallized grains and most of the grains have a high density of dislocations with a network structure. They suggested that, the presence of dislocation walls formed by the accumulation of dislocations indicates that recovery was incomplete during FSW, or was continuous in nature, and also that deformation was initiated by slip. However, due to lack of slip system in Ti, slip subsequently ceased and the alternative deformation mode, twin operated. In another study [15], authors argued that the existence of tangled dislocations is evidence for continuous or incomplete recovery during FSW of Ti. On the other hand, Zhang [17] reported that FSW of Ti results in only a slight occurrence of twins. In the present study, however, the grain structure contains a small number of twins (Fig. 1b). TEM examinations also revealed some twins in the microstructure of the pure Ti after FSP as well as in the nano-composites, for example Fig. 8a which illustrates a TEM image of the Ti–20n–0.8 sample showing a typical deformation twin with a width of approximately 300 nm. One should consider that Mironov [18] has noted that the grain structure evolution during FSP/FSW of Ti is a complex process driven mainly by the texture-induced grain convergence, but also involves the geometrical effects of strain and limited discontinuous recrystallization. Microstructure evolution will be more complex in nano-composite samples due to the presence of nano-particles. Most of the studies carried out on microstructure evolution of metal matrix nano-composites or microstructures containing nano-sized second phases pointed out the role of nano-particles to retard grain
Fig. 3. Field emission electron microscopy images showing the distribution of reinforcements in the matrix of samples: (a) Ti–80n–1.2; and (b) Ti–20n–1.2.

Fig. 4. Size distribution of particulate reinforcement in composites containing particles of 80 nm: (a) Ti–80n–0.8; (b) Ti–80n–1.2; and (c) Ti–80n–1.6; and composites containing particles of 20 nm (d) Ti–20n–0.8; (e) Ti–20n–1.2; and (f) Ti–20n–1.6.
boundary migration. Comparison of the mean grain size of nano-composite samples with that of Ti–4p sample in Fig. 2 supports the notion that the pinning effect of nano-particles on grain boundary movement contributes significantly during FSP. For example, Fig. 8b shows a bright field TEM image of Ti–80n–1.2 sample, where two marked nano-particles have pinned the grain boundary.

The volume fraction ($V_p$) and radius ($r_p$) of particles are two important factors in determining the equilibrium matrix grain size of composites containing particulate reinforcements. Zener [20] used these parameters to derive an equation for the critical matrix grain size by a simple approach to estimate the pinning pressure initially imposed by a distribution of particles. The Zener limiting grain size ($d_z$) can be calculated using Eq. 1 [20] as follows:

$$d_z = \frac{4r_p^3}{V_p} \left(1 \right)$$

According to the Zener pinning theory [20] a higher volume fraction or smaller particle size promotes a smaller limiting grain size. However the calculated Zener limiting grain sizes based on the volume fractions and mean cluster size values from Fig. 4 are not in agreement with the average grain sizes based on this equation (see Table 2). Rios [21] introduced another model to predict the final grain size during the grain growth in the presence of second phase particles. This model is based on energy dissipated during the motion of an interface through particle dispersion rather than the opposing force as was proposed by Zener. Rios parameter ($d_r$) represents the final grain radius and is defined by Eq. 2 as follows:

$$d_r = \frac{r_p}{6V_p} \left(2 \right)$$

Fig. 9 shows a diagram illustrating the relation between calculated grain sizes based on Rios parameter and measured mean grain sizes at different volume fractions. From this diagram, it is evident that the average grain sizes of the matrix tended to decrease substantially with increasing volume fraction. Furthermore, the average grain size values are in reasonable tolerable agreement with values deduced from the Rios equation. This agreement is more prominent in lower volume fractions, with higher deviations at increasing volume fractions. This is attributed to this fact that both Eqs. 1 and 2 are driven in a condition of
which particles are distributed ideally uniform, where they have maximum effect on pinning boundaries and refining of grain size. Departing from this condition causes a greater difference between actual and calculated values of grain size. As can be confirmed from the results of Fig. 4, with increasing volume fraction of particles, a wider spread of distribution in the cluster sizes is observed. In other words, higher volume fractions result in less homogeneity of the particles. Therefore, it can be described that the effectiveness of nano-particles on boundary pinning and grain refinement becomes weaker with increasing volume fraction, although a higher volume fraction results in smaller grain size.

4.2. Mechanical properties

The slight enhancement of hardness in pure Ti after FSP without Al2O3 nano-particles (see Fig. 5a) is correlated with the grain refinement due to restorative processes. It is well known that fine-grained FSP region has higher hardness due to the Hall–Petch
where $\sigma_f$ is the equation constant and samples results in much lower values compared to those of average particle distances ($\lambda$). In order to investigate the variation of hardness and yield strength values as a function of inverse of the square root of $\lambda$ and volume fraction ($\psi$) are two parameters needed to calculate $\lambda$ value using Eq. 4 [24]:

$$\lambda = d_p \left( \frac{\pi}{6V_p} \right)^{1/2} - 1$$

(4)

Fig. 10b shows that the mechanical properties, especially yield strength of nano-composites, are dependent on the average particles distance. However, the yield strength is inversely proportional to $\lambda$. Thus, mechanical properties of nano-composites are highly influenced by matrix grain size, and size, volume fraction and distribution of reinforcements. Contribution of each strengthening factor is discussed in the following section.

4.3. Strengthening mechanisms

As mentioned before, results show the correlation between microstructural characteristics and mechanical properties of nano-composite samples. Experimental results and the corresponding calculated data are summarized in Table 2. This section will investigate the contribution of each strengthening mechanism in increasing the yield strength of nano-composite samples by using current theories and data listed in Table 2. Then, a model for achieving the total strengthening expected from the presented mechanisms, and also for prediction of yield strength of composites using microstructural evidences will be proposed.

Hall–Petch theory (Eq. 3) explains the effect of grain refinement on improvement of yield strength. Values of $\sigma_f$ and $\kappa$ in Eq. 3 can be obtained from intercept and slope of fitted lines in Fig. 10a, respectively. These values are deduced as $\sigma_f = 286.7$ MPa and $K = 0.097$ MPa m$^{-1/2}$ in the unreinforced samples and $\sigma_f = 130$ MPa and $K = 0.305$ MPa m$^{-1/2}$ for composite samples. These values are somewhat different to those reported in previous research [25–27] due to variation in process and material composition. As discussed before, since the Hall–Petch equation is deduced from the fitted line of unreinforced samples to represent only the strengthening contribution of grain size, it is suggested that one may use a Hall–Petch equation derived from unreinforced samples to clarify the independent influence of grain refinement on strengthening of composite samples. Since the equation obtained from composite samples data supports the overall strengthening contributions, the Hall–Petch equation for composite samples is deduced as follows:

$$\sigma_f = 286.7 + 0.097(d)^{-1/2}$$

(5)

By using $d = 0.71 \times 10^{-6}$ m for Ti–20n–1.2 sample, yield strength value is deduced as ~402 MPa from Eq. 5; however the experimental value of yield strength is ~494 MPa that is about 92 MPa greater than the calculated value. This difference is likely caused by the other contributions to strengthening mechanisms besides grain refinement. Combination of Eqs. (2) and (5) and considering that the contribution of Hall–Petch strengthening ($\Delta\sigma_{HP}$) is equal to $K(d)^{-1/2}$

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Volume fraction of particles (%)</th>
<th>Average cluster size (nm)</th>
<th>Average particle distance (nm)</th>
<th>Zener limiting parameter (μm)</th>
<th>Rios grain size (μm)</th>
<th>Mean grain size (μm)</th>
<th>Hardness (HV)</th>
<th>Yield strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–80n–0.8</td>
<td>1.8</td>
<td>141</td>
<td>293</td>
<td>10.44</td>
<td>1.31</td>
<td>1.14</td>
<td>227</td>
<td>412</td>
</tr>
<tr>
<td>Ti–80n–1.2</td>
<td>2.9</td>
<td>151</td>
<td>245</td>
<td>6.94</td>
<td>0.87</td>
<td>0.93</td>
<td>276</td>
<td>436</td>
</tr>
<tr>
<td>Ti–80n–1.6</td>
<td>4.1</td>
<td>191</td>
<td>255</td>
<td>6.21</td>
<td>0.78</td>
<td>0.89</td>
<td>312</td>
<td>456</td>
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<tr>
<td>Ti–20n–0.8</td>
<td>2.2</td>
<td>103</td>
<td>193</td>
<td>6.24</td>
<td>0.78</td>
<td>0.81</td>
<td>239</td>
<td>452</td>
</tr>
<tr>
<td>Ti–20n–1.2</td>
<td>3.9</td>
<td>125</td>
<td>172</td>
<td>4.27</td>
<td>0.53</td>
<td>0.71</td>
<td>338</td>
<td>494</td>
</tr>
<tr>
<td>Ti–20n–1.6</td>
<td>5.7</td>
<td>166</td>
<td>182</td>
<td>3.88</td>
<td>0.49</td>
<td>0.88</td>
<td>383</td>
<td>479</td>
</tr>
</tbody>
</table>

Fig. 9. The relation between calculated grain sizes on Rios parameter and measured mean grain sizes at different volume fractions.

Fig. 10a shows the variation of hardness and yield strength as a function of inverse of the square root of grain size ($d^{-1/2}$) for both reinforced and unreinforced samples. It is clearly observed that, for all samples, grain refinement leads to enhanced mechanical properties. It should be emphasized that, in the case of composite samples, hardness data sets have several points that have a considerable difference to the trend line indicating that hardness data do not obey a linear behavior in comparison to the yield strengths data. However, in unreinforced samples, both hardness and yield strength values obey the Hall–Petch relationship [23]. The Hall–Petch equation is defined as follows:

$$\sigma_f = \sigma_0 + K(d)^{1/2}$$

(3)

where $\sigma_f$ is the final yield strength, $\sigma_0$ is the initial yield strength, $K$ is the equation constant and $d$ is the grain size. In Fig. 8a the slopes of linear fits give the values of $K$. It can be revealed that the slope of linear fit of yield strength values for unreinforced samples is much less than that of composite samples. In other words, extrapolation of this line to the smaller grain sizes (i.e. $d^{-1/2}$ range for composite samples) results in much lower values compared to those of composites samples. This difference clarifies the extra contribution of other strengthening mechanisms. In fact, these mechanisms are due to the presence of nano-particles. In order to investigate the independent role of nano-particles on improving mechanical properties, the variation of hardness and yield strength values as a function of average particle distances ($\lambda$) is plotted in Fig. 10b. Particle size ($d_p$) and volume fraction ($\psi$) are two parameters needed to calculate $\lambda$.
where the σ of composites (Contribution of Orowan mechanism in increasing the yield strength involving the interaction between dislocations and reinforcements. due to the presence of Al₂O₃ nano-particles in the composite reinforcements is the basis of another strengthening mechanism bearing mechanism in increasing yield strength (mechanism in metal matrix composites. The contribution of load transfer below for equiaxed particles:)

\[
\Delta \sigma_{\text{LP}} = 0.238 \left[ \frac{d_p}{V_p} \right]^{-1/2}
\]

Load transfer from compliant matrix to the stiff and hard reinforcements is the basis of another strengthening mechanism due to the presence of Al₂O₃ nano-particles in the composite samples. A modified shear lag model introduced by Nardone and Prewo [28] is usually considered to explain the load transfer mechanism in metal matrix composites. The contribution of load bearing mechanism in increasing yield strength (Δσ_{LB}) can be defined as follows:

\[
\Delta \sigma_{\text{LB}} = V_p \sigma_m \left[ \frac{(L + 2t)A}{4L} \right]
\]

where \( \sigma_m \) is the yield strength of the matrix, \( L \) is the particle’s dimension parallel to the load direction; \( t \) is the thickness of the particles and \( A = L/t \) is the aspect ratio. Eq. 7 can be modified as below for equiaxed particles:

\[
\Delta \sigma_{\text{LB}} = \frac{1}{2} V_p \sigma_m
\]

The Orowan mechanism is another strengthening factor that is involving the interaction between dislocations and reinforcements. Contribution of Orowan mechanism in increasing the yield strength of composites (Δσ_{OR}) can be determined according to Eq. 9 [23] as follows:

\[
\Delta \sigma_{\text{OR}} = \frac{0.13 b G}{d_p \left( \frac{1}{2V_p} \right)^{1/3} - 1} \ln \left( \frac{d_p}{2b} \right)
\]

where \( b \) is the burger vector (=0.347 nm for Ti [26]) and \( G \) is the shear modulus (=45.6 GPa for Ti [26]). For example, the calculated Δσ_{OR} for Ti-20n-1.2 sample from Eq. 9 is equal to ~ 64 MPa by using \( V_p \) and \( d_p \) values as 0.039 and 125 nm, respectively.

Enhanced dislocation density is the last presented strengthening mechanism in this study. This mechanism expresses that the difference between the coefficient of thermal expansion (CTE) between matrix and reinforcements generates thermal stresses around nano-particles due to the cooling from processing temperature. These thermal stresses cause plastic deformation of material nearby the nano-particles. Thermal stresses quickly reduce with increasing distance from matrix/particles interface and they can produce small discontinuities such as dislocations in the vicinity of nano-particles [29]. Two Al₂O₃ nano-particles and the generated dislocations can be observed in the bright field TEM image taken from the Ti-80n-0.8 sample. The effect of increasing dislocation density caused by CTE mismatching on strengthening of composites (Δσ_{T}) can be obtained using Taylor equation [30] as follows:

\[
\Delta \sigma_{\text{T}} = M\beta \sigma_b \sqrt{\rho^{\text{CTE}}}
\]

where \( M \) is the Taylor factor (=3.00), \( \beta \) is the equation constant (=0.20), and \( \rho^{\text{CTE}} \) is the dislocation density caused by CTE mismatching that can be obtained from Eq. 11 [30] as follows:

\[
\rho^{\text{CTE}} = A \Delta \alpha \Delta T V_p
\]

where \( \Delta \alpha \) represents the difference in CTE between matrix and particles. CTE values for pure Ti and Al₂O₃ particles are 8.5 × 10⁻⁶ k⁻¹ and 5.3 × 10⁻⁶ k⁻¹, respectively. The value of ΔT is the difference between processing temperature and testing temperature. In the present work, the maximum measured temperature during FSP was found to be ~870 °C. In addition, the testing temperature was 25 °C. The term \( A \) is a geometric constant in the range of 10–12 depending on particles’ geometry. For equiaxed particles, the value of \( A \) is considered to be 12 [30].

Fig. 11 reveals the contribution of each mentioned strengthening mechanism for all six composite samples. It can be clearly seen that the effectiveness of Hall-Petch mechanism (grain size) is much higher than the other mechanisms. In addition, the minimum contribution is related to load bearing effect.
Several models have been proposed in order to aggregate the micro-constituents and thereby to estimate the overall strength of particulate reinforced composites ($\sigma_c$) by considering the contribution of each strengthening effect. The simplest model applies the simple mathematical summation of all effects as follows:

$$\sigma_c = \sigma_0 + \Delta\sigma_1 + \Delta\sigma_2 + \Delta\sigma_3 + \ldots$$

(12)

Clyne [31] suggested another model in which root of the sum of squares was used to aggregate the strength contributions into an overall strength as follows:

$$\sigma_c = \sigma_0 + \sqrt{\Delta\sigma_1 + \Delta\sigma_2 + \Delta\sigma_3 + \ldots}$$

(13)

In the simple summation model it is assumed that the effect of each mechanism is independent of the other mechanisms; however in Eq. 13, the contribution of each factor is taken into account along with the effect of other factors.

Ramakrishnan [32] supposed an analytical model for predicting yield strength by incorporating load transfer mechanism (Eq. 7) and CTE mismatching effect (Eq. 10) as follows:

$$\sigma_c = \sigma_0(1+f_{LB})(1+f_{CTE})$$

(14)

In this model, $f_{LB}$ is the improvement factor relation to load bearing mechanism and is defined as $\Delta\sigma_{LB}/\sigma_0$ and $f_{CTE}$ is the improvement factor of increasing dislocation density caused by CTE mismatching and is equal to $\Delta\sigma_{CTE}/\sigma_0$. In this model the other effects such as Hall–Petch and Orowan mechanisms are not considered. Zhang and Chen [33] modified the Ramakrishnan model by adding the Orowan effect to Eq. 14, though the Hall–Petch effect was not taken into account, which would predict under estimated values. In the present work, it is clear that grain refining has the most significant effect rather than the other mechanisms. Ramakrishnan model can be modified by incorporation of Orowan and Hall–Petch effects as follows:

$$\sigma_c = \sigma_0(1+f_{LB})(1+f_{CTE})(1+f_{HP})(1+f_{OR})$$

(15)

Fig. 12 shows a diagram of calculated yield strength values using the mentioned models versus experimental ones. The diagonal line plotted in this diagram represents the points on which the experimental data and theoretical values are identical. It can be observed that the modified Ramakrishnan model and simple summation model result in greater values than those of the experimental ones. In addition, the calculated values from Clyne and Zhang models are lower than those of the experimental ones. Among these models, Clyne model is in best agreement with the experimental results. Therefore, this model appears to be the best for the prediction of the yield strength of Ti/nano-alumina composites produced by FSP. For comparison, the numerical results of Clyne model are shown in Fig. 13 for various nano-particle sizes and volume fractions.

Fig. 13a illustrates that strengths dramatically increase to an amount of ~1000 MPa when 25 nm particles are used with a volume fraction of ~10%. Fig. 13b suggests that a mean particle size of less than 50 nm will promote dramatically higher yield strengths.

5. Conclusions

This work has examined the contributions of particle size and volume fraction of reinforcements in FSP fabricated Ti/Al2O3 nano-composites. The introduction of nano-scale reinforcing particles has dramatically reduced Ti matrix grain size to ultra-fine range. The trend in grain size reduction was found to be best described by the Rios equation rather than the Zener pinning model. The yield strength of the nano-composites increased from ~351 MPa in pure Ti after FSP, to ~494 MPa when 20 nm-Al2O3 particles are dispersed through the Ti matrix. Based on the analysis of the yield strength contributions through grain refinement, load transfer, Orowan looping, and CTE mismatch effects, it was found that the Hall–Petch effect makes the greatest contribution to the yield strength due to the significant grain refinement observed.
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