STRUCTURAL EVOLUTION OF AL-20% (WT) AL_2O_3 SYSTEM DURING BALL MILLING STAGES

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Abstract Production of nanostructured aluminum matrix composite powder by high energy ball milling is investigated. Scanning electron microscopy analysis as well as the tap and green density measurements were used to optimize the milling time needed for the completion of the mechanical milling process. Also, we studied the particles morphology and size distribution change with milling time and its correlation with pressability and tap density. SEM showed that distribution of alumina particles in the Al matrix reaches a full homogeneity after the steady state. This would increase the hardness of powder due to a nano-structured matrix and oxide dispersion strengthening.

Keywords Metal-Matrix Composites, Nano-Structured Materials, Steady State

چکیده در این پژوهش، تولید کامپوزیت نانوساختار زمینه آلومینیوم توسط آسیاب پر انرژی مورد مطالعه قرار گرفت. میکروسکوپ الکترونی روبشی و دانسیته ضربه ای و دانسیته خام برای تعیین زمان بهینه فرایند آسیاب مورد استفاده قرار گرفتند. نتایج نشان دادند که مورفولوژی و توزیع اندازه ذرات با زمان آسیاب تغییر می‌کنند که این تغییرات رابطه نزدیکی با قابلیت پرس و دانسیته ضربه ای دارد. نتایج میکروسکوپ الکترونی نشان دادند که توزیع ذرات آلومینا در زمینه با زمان پایا برای آسیاب رابطه نزدیکی دارد. همچنین سختی پودر با توجه به ساختار نانو و توزیع ذرات اکسیدی به میزان قابل توجهی افزایش یافته است.

1. INTRODUCTION

Aluminum alloys are important structural materials, but for many applications it is still necessary to improve their mechanical properties. The incorporation of ceramic particulates in Al or its alloy matrices increases the elastic modulus and yield strength by the Orowan strengthening effect [1-3].

A survey of the previous works indicates that homogenous dispersion of fine particles in a fine grained matrix is beneficial to the mechanical properties of MMCs [1,3-6].

Ball milling is a simple and useful technique for attaining a homogeneous distribution of inert fine particles within a fine grained matrix. Addition of ceramic reinforcements into a ductile matrix has a great effect on structural evolution during ball milling. Previous researches focused on addition of low percentages of ceramic phases to Al matrix by mechanical alloying [7-13]. This study shows that addition of 20 % wt Al_2O_3 markedly influences the structural evolution of the Al matrix during milling stages. The time needed to reach the steady state, also depends on distribution of alumina particles in the Al matrix. In spite of the absence of alloying elements, the ultimate powder has an excellent hardness and acceptable morphology for the powder metallurgy process.

2. EXPERIMENTAL PROCEDURE

High purity Al powder (Merck, Art. No: 1056) as a monolithic system and a mixture of Al-20 % (wt) alumina powder (Martinswerk, MR70, d50: 0.5-0.8 μm) were seperately milled in P5 planetary mill for various periods of time up to 25 h. Ball to powder ratio was about 15:1 and the mill speed maintained at 250 RPM. 3 % (wt) of stearic acid was added to retard excessive welding. The milling atmosphere was Ar which was purged into cups before milling. Product sampling was performed in the glow box in the Ar atmosphere to prevent oxidation. The powder produced after different stages of milling was examined using a Cambridge Scanning Electron Microscope (SEM) operating at a voltage of 30 KV.

The X Ray Diffraction (XRD) patterns were taken using a Siemens X ray diffractometer (30 KV and 25 mA) with Cu Kα radiation. Grain size and lattice strain changes during milling stages calculated by the Williamson-Hall method for at least three peaks [14]: $B \cos \theta = 0.9 \lambda/D + 2 \eta \sin \theta$ where B, λ, θ, D and η are FWHM, wave length, peak position, crystallite size and lattice strain, respectively. Powders were mounted and polished to be prepared for microhardness test. To study the green density changes, the powder was first pressed by isostatic press (500 MPa) and then the BS1902A standard was applied.

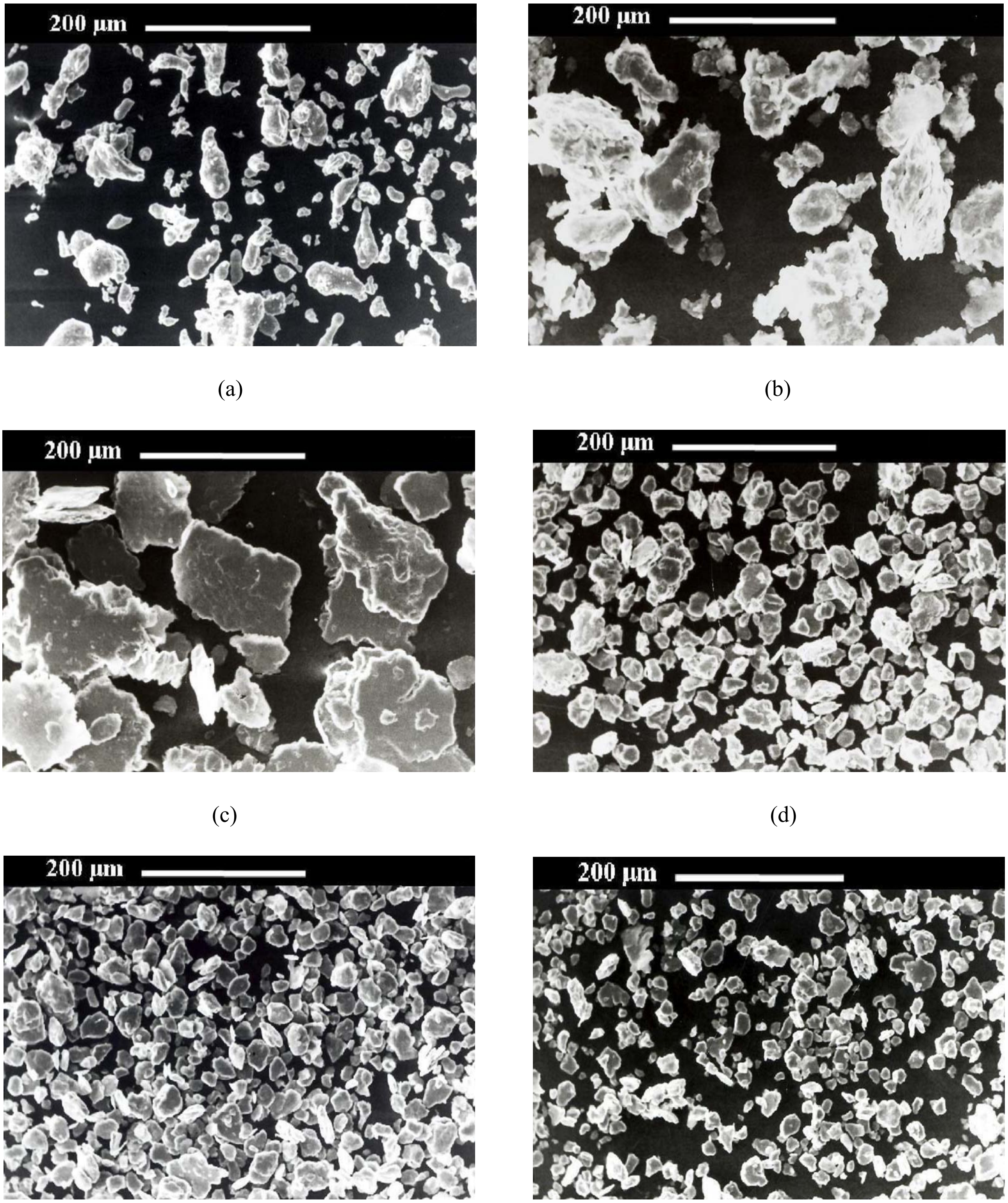
3. RESULTS AND DISCUSSION

3.1. Morphological Changes The as received atomized Al powder (Figure 1a) is predominantly equiaxed. Powder particles deform into a flaky like shape by milling up to 5 h (Figure 1b). Due to the ductile nature of aluminum powder, welding is the dominating mechanism in this stage [15], so the 10 h milling product has large size and flattened shape as shown in Figure 1c. The plate like particles work hardened after 15 h milling, thus fracture mechanism is activated. (Figure 1d). Flake-like morphology is maintained after 15 h milling but the particle size distribution changed and the average particle size is decreased. Indeed, large flake like particles are crushed by intensive impacts. At 20 h, lower aspect ratio can be seen and size distribution has a narrow range (Figure 1e). Further milling up to 25 h has no effect on morphology (Figure 1f); indeed at milling times longer than 20 h, the steady state predominates. It is important to note that after stabilizing the size of the powder, their microstructure refinement can still take place and terminate later [16].

Figure 2 shows the morphology of the mechanically milled Al-20 % (wt) Al_2O_3 powder. Considering the changes of morphology; one may notice the effect of reinforcement addition on the MA process [10]. Despite the ductile nature of Al powder, formation of large flaky like particles is prevented by presence of alumina particles.

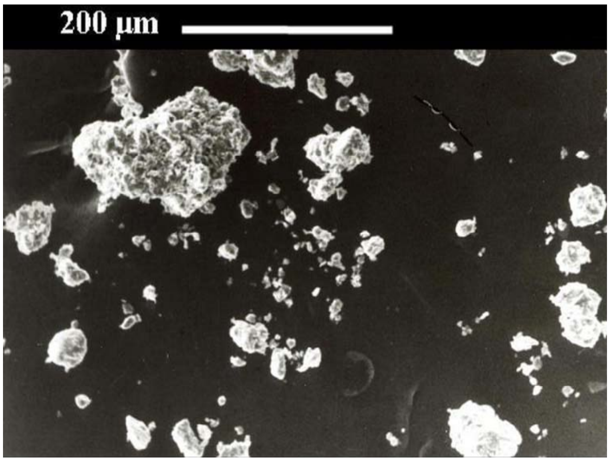
After 5 h milling (Figure 2a), powder has a broad distribution of irregular particles with a slight aspect ratio. Because of soft Al matrix, cold welding is the predominant mechanism at this stage which result in large. Figure 2b shows a typical large particle consisting smaller microwelded particles. Each of these large particles will be fractured by more intensive impacts due to work hardening of Al matrix. With increasing milling time to 10h (Figure 2c), work hardening activates the fracture mechanism and the particle size distribution is limited. In the case of reinforced Al, neither the plate like particles nor the laminate appeared. Presence of the alumina particles in the Al matrix decreases ductility; so fracture occurs before lamination [17]. With 15 h milling time (Figure 2d), particles shape and size distribution are stabilized. Further milling up to 20-25 h, makes no significant difference. Other authors have reported that the presence of ceramic particle reinforcement accelerates the kinetic of the process [17,18]. This affirmation was made on the correlation observed between tap density and milling time, explained by the morphological and microstructural evolution of the powder particles which is also in agreement with this study. For the monolithic Al, ball milling process is completed in 20-25 h milling while it is 10-15 h for the reinforced matrix. The presence of alumina particles increases local deformation which improves the work hardening and thus fracture mechanism is activated in less time. Indeed small hard and brittle particles in the matrix act as small milling agents, thus the steady state milling time is reduced [18].

3.2. Structural Evolution The effect of milling time on the distribution of Al_2O_3 particles is examined by SEM. Figure 3a shows the distribution of reinforcement particles resulting from a simple mixing method (0 h milling) which is known as the routine powder metallurgy process.

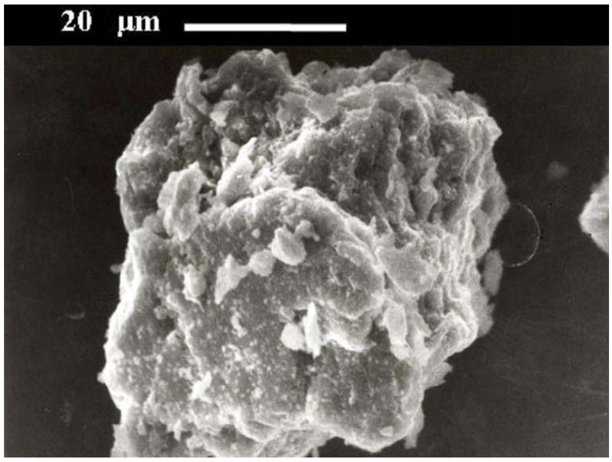


(a) (b) (c) (d) (e) (f)

Figure 1. The effect of milling time on morphology of monolithic Al after (a) 0 h, (b) 5 h, (c) 10 h, (d) 15 h, (e) 20 h and (f) 25 h.



(a)



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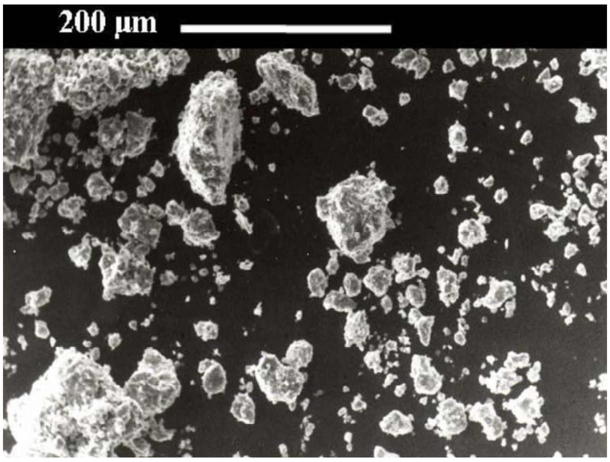

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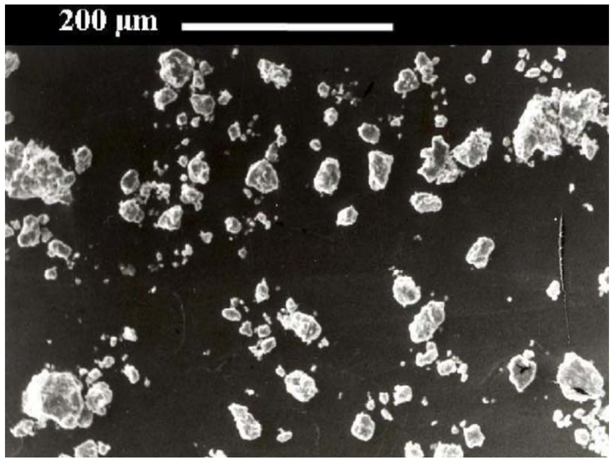
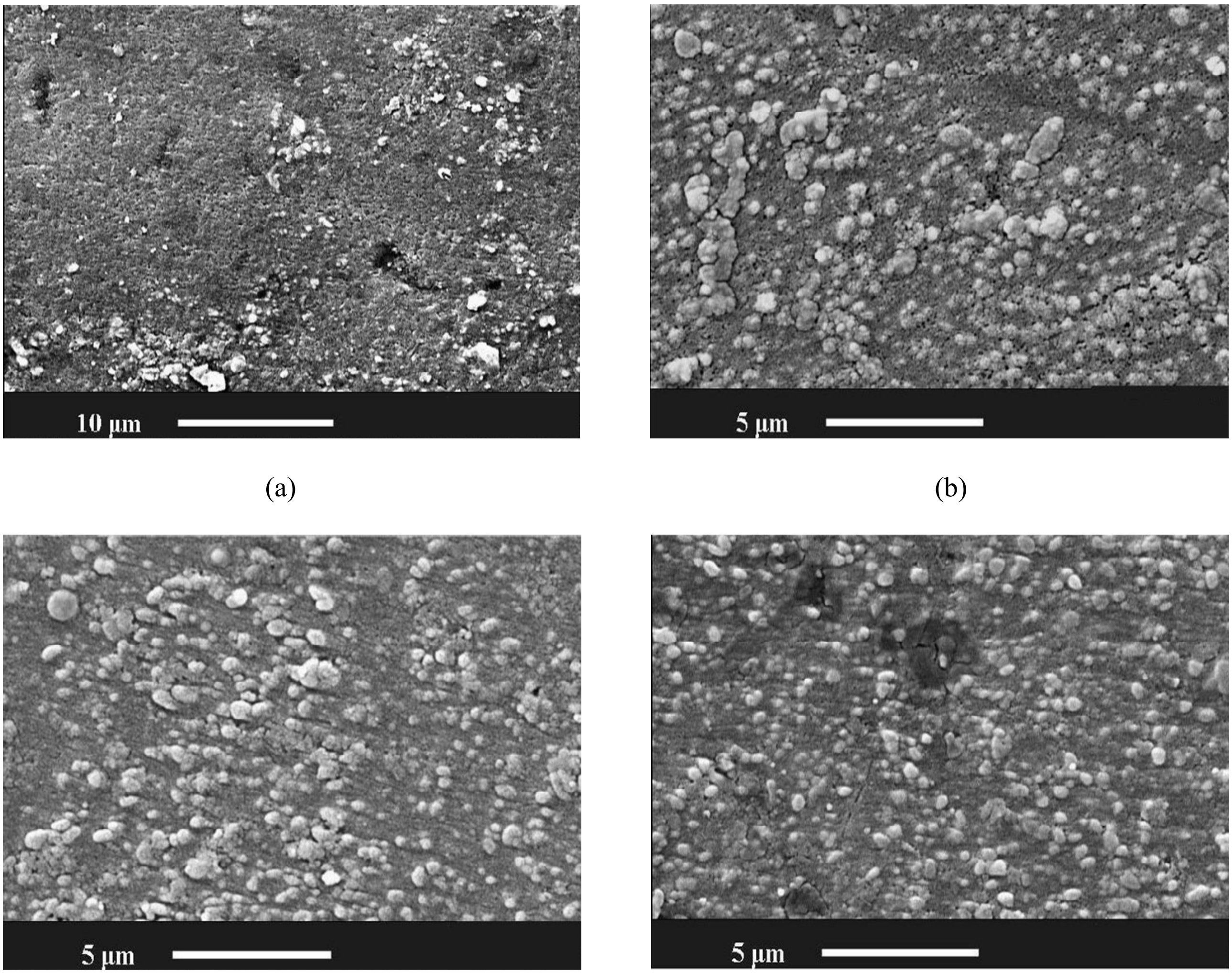


(d)

Figure 2. The effect of milling time on morphology of composite powder after (a,b) 5 h, (c) 10 h and (d) 15 h.

The reinforcement particles adhere together and the result is the heterogeneous distribution of Al_2O_3 particles. By milling up to 5 h (Figure 3b), these particles spread throughout the Al matrix with a better homogeneity, though clustering is still seen in some areas. Milling time longer than 10 h provides a homogeneous distribution of reinforcement particles (Figure 3c) and prolonged milling has no noticeable effect (Figure 3d). Comparing Figure 2 and 3, steady state has a strong dependence on the distribution of alumina particles in the Al matrix. Accordingly, steady state is attained only after full homogenization of the reinforcement particles in the matrix has occurred.

Considering the initial size of alumina particles (D_{50}: 0.5-0.8 μm) it is clear that these particles did not crush markedly during intensive impacts of balls. α-alumina is the most stable oxide of aluminum, and the phase diagram indicates that no other compound can be formed at the Al/Al_2O_3 interface [5,19]. The only probable reaction at the interface is alumina dissolving in the Al and/or formation of thin amorphous alumina layer at



(a) (b) (c) (d)

Figure 3. Distribution of alumina particles in Al matrix with milling time after (a) 0 h, (b) 5 h, (c) 10 h, (d) 15 h.

interface [20]. In this work, however, alumina particles seems to have engaged in Al matrix mechanically and formation of chemical interface seems unlikely.

Figure 4 shows the tap density dependence on milling time for the monolithic and reinforced Al. It should be noted that tap density depends only on the shape and size of powder particles and not on micro-structural properties of powder. For monolithic Al, three stages can be seen; declining, increasing and steady state. With short milling times, there is a continuous decrease in the tap density with a minimum between 5-10 h. This reduction is ascribed to formation of large flake like particles (as shown in Figure 1b) and consequently the worst packaging properties of the powder [21]. With further milling, powder particles are work hardened and fractured, so quasi spherical particles are produced and packaging properties improves. Between 20-25 h milling, no change in tap density is seen which as confirmed by SEM images, is the result of the steady state. For composite powder, milling time up to 15 h increases tap density continuously due to large particles fragmentation. Between 10-15 h, slope of diagram diminishes and after 15h tap density does not change vs. miling time. As shown by SEM images, 15 h is adequate for reinforced Al to achieve steady state.

It is that any changes in powder morphology has a great effect on packing characteristics of powder. In the case of bulk density and pressability, both the morphology and hardness of powder are effective. The green density curve of monolithic Al (Figure 5) is analogous to the tap density curve, having three stages due to powder morphology and particle size changes [15,22]. Though particles have a quite similar morphology at the start and end of the process, high plastic deformation reduces pressability and so causes lower green density for final monolithic Al powder [21]. On the other hand, decomposition of PCA into nano-particles of Al oxide and carbide increases the hardness of matrix and thus pressability. Furthermore, adherent aluminum oxide as a thin brittle layer on the surface of the particles retards cold welding in the particles [23]. For the composite powder, density versus milling time varies with a different regime, i.e. first decreasing and then stabilizing. The fact that the energy needed to crush the particles increases with decreasing particle size as well as work hardening and adherent oxide film on the aluminum particles, explains why the curvature tends toward zero with time. After 10-15h milling, green density becomes fixed due completion of the milling process. As

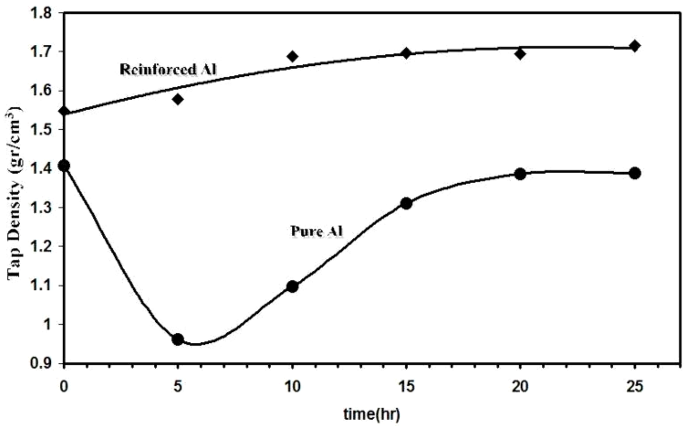


Figure 4. Tap density versus milling time for monolithic and reinforced Al.

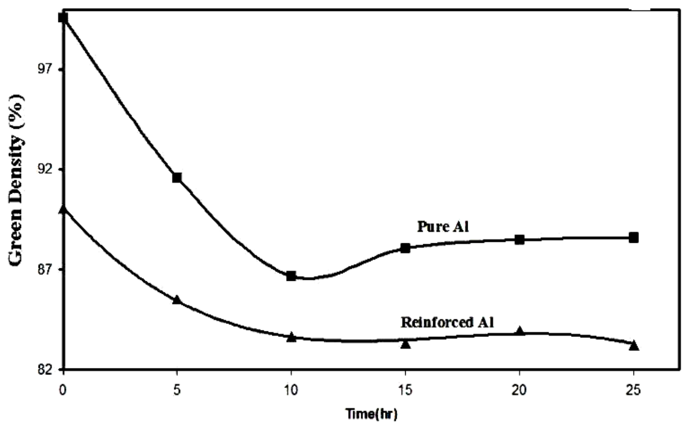


Figure 5. Green density versus milling time for monolithic and reinforced Al.

can be seen from the study of the changes of morphology and tap density vs. milling time, it can be deduced form the green density result that steady state time is reduced at the presence of ceramic particles [10,18].

The result of (111)/(200) intensities in the XRD patterns at different milling times is shown in Figure 6. Observing these curves, it is reasonable to assume three periods for MA of the monolithic Al, in a manner similar to the density curves. This can be understood considering the anisotropy in the elastic module of single-crystal Al. Therefore, grains within the powder particles are deformed into thin layers in the 'soft' direction, perpendicular to the direction in which the powder particles were flattened by milling ball. When the sample is prepared to perform the powder XRD analysis, this flattened powders and its (200) planes are arranged parallel to the sample-holder and as a consequence I_{200} increases whereas I_{111} decreases. With further milling, flattened particles are fractured and divided to equiaxial particles. Therefore particles lose their texture or preferential orientation and their reflection planes randomly arranged again and I_{111} recover its significance [17,21]. The result of dividing the principal (111) and secondary (200) reflections of reinforced Al has no marked change during milling stages, confirming lack of lamination for Al in the presence of alumina particles.

Figure 7 shows grain size and lattice strain of

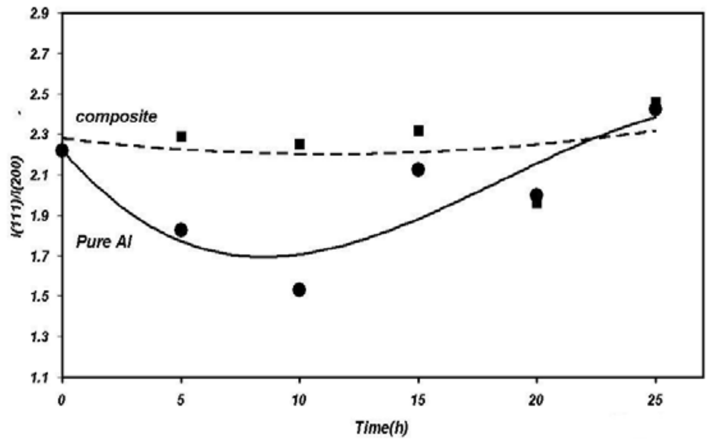


Figure 6. The effect of milling time on the I_{111}/I_{200} ratio of al.

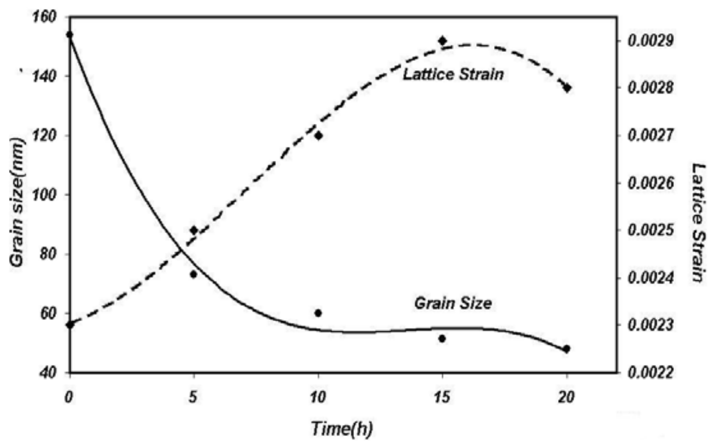
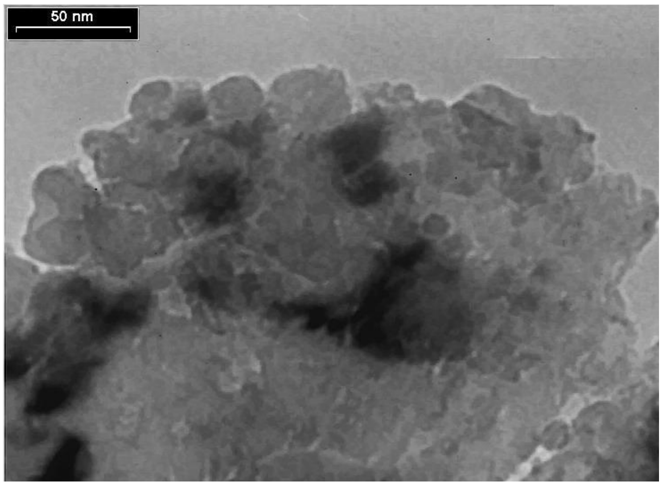


Figure 7. Grain size and lattice strain of monolithic al versus milling time.

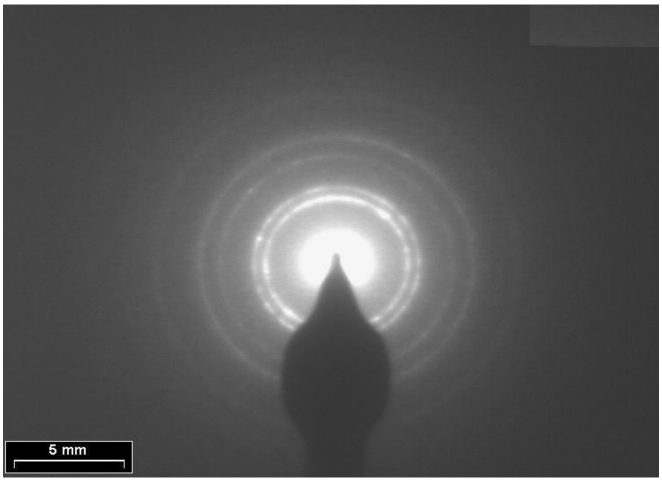
monolithic Al vs. time by Williamson-Hall method. Analytical models predicts that grain size decreases by milling time according to the equation $D = Kt^{-2/3}$, where K is a constant [12]. Considering the power of time, one can anticipates that the reduction of grain size occurs at the first milling stages. In this work, grain size decreases rapidly in the early stage of MA and then it is fixed about 46 nm. Lattice strain increases with time due to distortion effect caused by dislocation in lattice. Lattice strain curve has a maximum [17,24,25] which is ascribed to grain size reduction and its effect on strain reduction. With short milling time, severe plastic deformation causes a deformed lattice with high density of dislocations. By further milling a nano-grain structure is attained, so dislocations reach readily to the grain boundaries, causing diminution of total lattice strain [26].

TEM image of 25 h milled powder confirms the results obtained by Williamson-Hall method (Figure 8a). These fine grains create many spots in selected area electron diffraction pattern resulting a ringed shape SAED (Figure 8b).

Contamination caused by milling media is



(a)



(b)

Figure 8. (a) Bright field (b) Dark field and (c) SAED of al powder milled for 25 h.

known as another important structural change which usually occurs during milling. EDS analysis show that induced Fe contamination in monolithic Al system is negligible. However, presence of erosive particles in Al-Al_2O_3 system induced Fe as a major contamination (Table 1).

The nanostructured Al matrix influences strength according to Hall-Petch equation [27,28]. Modified Hall-Petch formula has been proposed in the form of $H = H_0 + KD^{-1/2}$ where H_0 is hardness of the annealed coarse grained sample, K is a constant and D is size of crystallite [29,30]. It is clear that the hardness of both monolithic Al and composite increase with milling time (Figure 9). Since strengthening due to grain size and the strength contribution caused by oxide dispersion can be additive [7,19], the curves of monolithic Al and composite are almost parallel. Furthermore, decomposition of PCA into C and O elements together with formation of ultrafine oxides and carbides improve the hardness of powder. The hardness of final powder is 180Hv which is about 6 times the initial powder.

4. CONCLUSION

Powder characterization of monolithic Al and Al-20 % (wt) Al_2O_3 mixture during ball milling stages was investigated. Addition of alumina powder has a great influence on the morphological characteristics as well as on decrease in steady state time. This affirmation is based on the observed correlation between density and milling time, explained by the morphological and microstructural evolution of the powder particles. Distribution of alumina particles within Al matrix reaches a full

TABLE 1. Effect of Milling Time on the Percentage of Fe Contamination Caused by Milling Media in Al-Al_2O_3 System.

Milling Time (h)	Fe Percent
0	0.42
5	1.49 ± 0.53
10	1.786 ± 0.35
15	2.018 ± 0.4
20	2.48 ± 0.17
25	2.65 ± 0.47

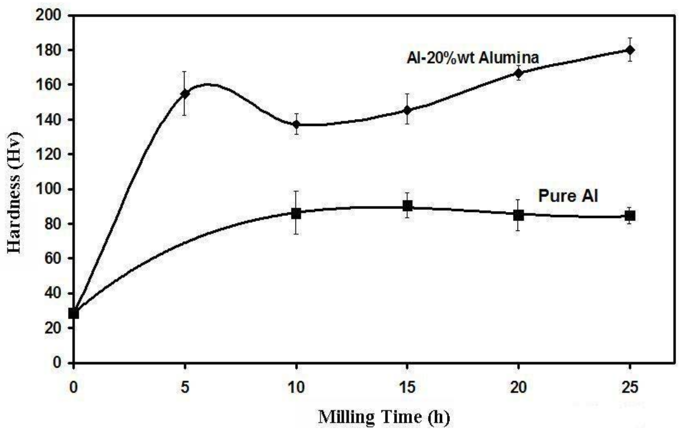


Figure 9. Powder hardness of monolithic and reinforced Al versus milling time.

homogeneity after steady state. The ultimate nanostructured matrix and homogenous distribution of reinforcements increase the hardness from 28.5 to 180 Hv.

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