Influence of Milling Time on the Microstructure and Mechanical Properties of Nanostructured Al–7% Si alloy

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Abstract— The microstructure and mechanical properties of Al–7% Si alloy prepared by ball milling technique under different milling time were studied. The results indicate that the grain size decreases with increasing the milling time, the average dislocation density, \( \rho \), was found to exhibit a drastic increases by increasing the milling time, the median diameter, \( \mu \), decreases, while the value of width parameter, \( \sigma \), is approximately constant with increasing the milling time. The value of Vickers hardness (HV) increases by increasing milling time, this increase was attributed to the refinement of grains with increasing milling time.

Index Term— Ball milling, Nanocrystalline, Microstructure, Microhardness and Al–Si alloys.

1. INTRODUCTION
Al–Si alloys are widely used because of their low density, good castability and high strength at elevated temperatures. They suffer, however, from low ductility or toughness, which limits their use to applications where these properties are not important [1], [2]. Hypereutectic Al–Si alloys have been applied in automobile engine cylinders, cylinder heads, pistons and cylinder liners, etc. [3]–[6]. The brittleness of coarse Si crystals is the main reason responsible for the poor properties of Al–Si alloys because coarse Si crystals lead to premature crack initiation and fracture in tension. Therefore, many efforts have been made in the microstructural modification of casting Al–Si alloys in order to achieve fine Si phases with beneficial shapes and distributions through, for instance, promoting heterogeneous nucleation and preventing growth of Si crystals by alloying additions [7]–[9]. There has been a continuous effort over the past years to enhance mechanical properties by changing solidification conditions, using additional heat treatments or introducing alloying elements to modify the Si particle morphology [1], [2]. The effects of high temperature diffusion treatment on the microstructure, mechanical properties, thermal extension and conduction have been studied [10]. The effects of geometrically necessary dislocations, processing temperature and die angle on the grain microstructure produced by severe deformation of Al–7% Si alloy have been discussed [11], [12].

Nanocrystalline materials are characterized by grain sizes in the range of a few nanometers and a high density of grain boundaries (about \( 10^8 \) m\(^{-2} \)). The finite crystal size, as well as the structure and the properties of the grain boundaries, strongly affect the properties of such materials [13]. Ball milling is an efficient and simple method for the fabrication of sub-micron or nanostructured powder materials, especially for manufacturing of some composite powders [14]. There are different types of ball milling methods based on the movement of milling balls and vial, such as vibration mill and planetary mill. In the case of planetary ball milling, main factors that affect the particle size reduction include rotation speed, size of balls, weight ratio of balls to powder, medium of milling, milling time etc. Because of the variety of the powder materials, the selection of parameters varied substantially [15]–[17]. The present study was carried out to report the preparing of nanostructured Al–7% Si alloy by ball milling method and studying the effect of milling time on the microstructural and mechanical properties of the prepared alloys.

2. EXPERIMENTAL DETAILS
A hypoeutectic Al–7 wt. % Si alloy was prepared at Central Research Laboratory of Aluminum Egypt Company. Nanocrystalline Al–7 wt. % Si alloy was synthesized by ball milling technique- for more details about the used technique you can see [18]. The milling time was adjusted to be 12, 24, 48 and 72 h, respectively. This rendered a ball–to–charge weight ratio of around 6:1.

The microstructure of nanocrystalline Al–7 wt. % Si alloy was performed by using a Phillips X-ray powder diffractometer coupled with a Philips X-ray generator (PW 1730) the operating parameters were shown in details in [19]. The recorded X-ray diffraction spectra were used to calculate the grain size and dislocation structure from the profile breadth. The profile breadth was calculated by computer software after automatic background removal and \( k_{\alpha 2} \) stripping (stripping ratio \( k_{\alpha 2}/k_{\alpha 1} = 0.51 \)).

The micro-hardness of compacted alloys was investigated by continuous Vickers hardness test. During the test a Vickers pyramid was pressed into the surface of the sample by hydraulic mechanical testing machine (MTS 810), which was
controlled by computer. During the loading period the Vickers pyramid penetrated into the surface of the sample at constant velocity and the same velocity was applied in unloading period when the pyramid moved backwards. In the course of the test the load was registered as a function of the penetration depth.

3. RESULTS AND DISCUSSION

3-1. Lattice parameters

Figure 1 shows the X-ray diffraction of nanocrystalline Al-7 wt.% Si alloys at different milling time. It can be seen that, all the X-ray patterns characterized by four mean peaks (111), (200), (220) and (311) which refer to α-Al phases. In addition there are three peaks located at 2θ = 34.5°, 39.6° and 69.4° which refer to diamond Si. This result is in a good agreement with the previous studies of the optical micrographs of Al-Si alloys [20]. The Bragg’s peaks intensities decreases with increasing milling time and considerable line broadening can also be observed.

The lattice parameter of α-Al, a in nanocrystalline Al-7 wt.% Si alloys has been calculated as a function of milling time by plotting the lattice parameter, a_{0d} (calculated from the Bragg’s Law) against an extrapolation function

\[ F(\theta) = \frac{1}{2} (\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta) \]

which holds quite accurately down to low values of \( \theta \) [18, 21]. It could be noticed from Fig. 2 that, by increasing the milling time the value of lattice parameter increases to approach the value of pure Al lattice parameter which is 4.0496Å [22]. The slight increase of the lattice parameter interpreted to the formation of antisite-atom pairs [18].

3-2. Grain size and dislocation parameters

The modified Warren –Averbach procedures allow the precise determination of i) the average grain size, ii) the dislocation density \( \rho \), iii) the distance between adjacent dislocations, \( L_c = 1/\rho^{1/2} \) and iv) the dislocation arrangement parameter, \( \beta = \rho^{1/2}R \). The modified Warren –Averbach procedures is given by [23, 24]:

\[ \ln A(L) = \ln A'(L) - (\Pi b^2/2)P L^2 \ln (R/L)(k^2C) + O(k^4C^4) \]  

Where L is the Warren length, k is the diffraction vector, b is the length of burgers vectors, C is the contrast factor of the dislocations and O stands for higher order terms in \( k^2C^2 \).

The average values of dislocation contrast factor for screw dislocation in fcc-Al has been calculated according to [18, 23, 24].

\[ C = C_{0d} (1-q H^2) \]

Where \( H^2 = (h^2k^2+h^2l^2+k^2l^2)/ (h^2+k^2+l^2) \), \( C_{0d} \) is the dislocation contrast factor corresponding to the (h00) reflection plane and q is the dislocation character. The values of \( C_{0d} \) and q has been calculated from the elastic constant of aluminum \( \{c_{11} = 107 \text{ Mpa}, c_{12} = 60.8 \text{ Mpa and } c_{44} = 28.3 \text{ Mpa} \} \). The average values of contrast factor for screw dislocations, \( C_{screw} \), for (111), (200), (220) and (311) reflections in fcc-Al were used in the modified Warren – Averbach method.

Figure 3 shows the logarithms of the real part of the Fourier coefficient, \( \ln A(L) \), against \( k^2C \) for different L values for Al-7wt. %Si alloy (in the case of 48 hour ball milling as a representative example). From the figure we can notice that the values of \( \ln A(L) \) decreases with \( k^2C \) indicating the presence of lattice distortions. The \( \ln A(L) \) values flow a smooth linear relationship, indicating that the second order term in eq. (2) can be neglected.

The intercept of the fitted straight line at \( k = 0 \), yield the sequence of \( \ln A'(L) \) size coefficient while the slope yields M \( (L) = (\Pi b^2/2) L^2 \ln (R/L) \). In figure 3, the series of size coefficient, A' (L), were plotted as a function of L for Al-7wt. %Si (in the case of 48 hour ball milling as a representative example). The area weighted column length, \( <L_{area}> \), is given by the tangent to small L values of A' (L) extrapolated to the x-axis, while the volume average column length, \( <L_{vol}> \), can be determined from the area under the curve of A' (L) against L. The primarily obtained average column length of an ensemble of particles can be transformed into average grain size if all the crystallites in the sample have the same shape [18]. The area – weighted average grain size \( <D_{area}> \) and the volume –weighted average grain size, \( <D_{vol}> \) are given by [26]:

\[ <D_{area}> = 3/2 <L_{area}> \quad \text{and} \quad <D_{vol}> = 4/3 <L_{vol}> \]  

The volume weighted average grain size, \( <D_{vol}> \) and the area weighted average grain size, \( <D_{area}> \), are characterized by the median diameter, \( \mu \), and the geometrical standard deviations, \( \sigma \). [26]

The results in table I indicate that, the median diameter, \( \mu \) decreases with increasing the milling time, this result consistent with the published result [18]. While the values of width parameter, \( \sigma \) approximately constant, this result is in a good agreement with the previous studies [18, 19, 27]. They reported, that the values of \( \sigma \) of nanocrystalline materials dependent on the synthesis method. Typical \( \sigma \) are larger than 2 for nanomaterials prepared by ball milling.

The investigated values of \( <L_{area}> \), \( <L_{vol}> \), \( <D_{area}> \), \( <D_{vol}> \), \( \mu \) and \( \sigma \) as a function of milling time, \( \tau \), are listed in Table I. It can be seen that, both the area weighted column length, \( <L_{area}> \), and the volume weighted column length, \( <L_{vol}> \), decreases with increasing milling time. The ratio \( <L_{vol}> / <L_{area}> \) nearly constant for all milling time, equal to 1.8, while the ratio \( <L_{vol}> / <L_{area}> \) varies between 1.4 and 1.75 for Al powder [28].

The average volume grain size, \( <D_{vol}> \) decreases from 84.36 to 61.08 nm by increasing the milling time. Such a refining effect of ball milling has been reported previously for microstructure of this type [22]. The obtained values can be concluded that our alloys still in the nanocrystalline state, where nanocrystalline materials are single or multi-phase (poly-crystals) with grain size in the nanometer region (typically less than 100 nm in at last one dimension) [29].

The dislocation structure can be determined from the slope M \( (L) \) which can be written in the following form:

\[ M (L)/L^2 = (\pi b^2/2) \rho \ln \Re - (\pi b^2/2) \rho \ln L \]
The obtained values of \( \rho, L_c, R_e \) and \( \beta \) as a function of milling time, were listed in Table I. The average dislocation density, \( \rho \), was found to exhibit a drastic increase from 7.2 x10^{14} \text{m}^{-2} \) to 22.2 x10^{14} \text{m}^{-2} \) by increasing the milling time as shown in Table I.

The average distance between adjacent dislocations, \( L_c \), decreases with increasing milling time. The dislocation distance is only by a factor (0.83 - 1.08) greater than the characterized \( <L>_{\text{area}} \), i.e. the individual nanograin contains just a few dislocation. According to this, the second term in Warren-Averbach analysis, corresponding to the dislocation interaction was negligible [23].

Also from table I it can be seen that the values of dislocation arrangement parameter, \( \beta \), increase with increasing milling time refer to the strength of the dipole character and the screening of the displacement filed of dislocation is strong which means strong correlation in the dislocation distribution with milling time [18, [19].

Figure 6 shows the dislocation density, \( \rho \), varies inversely with the average volume grain size \( <D>_{\text{vol}} \). Similar relationship was observed previously for nanocrystalline Al-based powders [23], this phenomenon is interpreted to the strain resulting from the defects in the grain interior, and the strain resulting from grain boundaries [30].

### 3-5. Micro-hardness

In most cases, superior mechanical properties are needed for industrial applications. Since strength and hardness of the alloys are mainly dependent on its microstructure, much effort has been devoted to refining the grains of the alloy in order to improve the mechanical properties [31, 32].

The hardness of compacted nanostructured Al - 7 wt. % Si for different ball milling time has been investigated by Vickers hardness test. The average values of Vickers hardness (HV) for average ten runs are listed also in Table I. From Table I, It could be noticed that, the value of Vickers hardness (HV) increases from 556 ±20 Mpa to 590 ±20 Mpa by increasing milling time, this increase can be attributed to the refinement of grains with increasing milling time [31 – 35].

To verify the relation between microhardness and grain size we extend our work to study the Hall – Petch (H-P) relation. The H- P relation is obeyed fairly well in crystalline materials with grain sizes ranging from tens of nanometers to microns. It often fails, however, in alloys with grain sizes in the range 3 – 20 nm [36]. Figure 7 shows H-P plot of microhardness (HV0.01) versus inverse root of grain size for compacted nanocrystalline Al - 7 wt. % Si alloys. The best fit line describes the H-P dependence of microhardness (HV0.01) on the grain size for our alloys, in the following form:

\[
\text{HV0.01} = 388 + 1587 (\langle<\text{D}>_{\text{vol}}\rangle)^{-0.53} \text{(Mpa)}
\]

The correlation coefficient R = 0.794, the fit is still quite reasonable and most importantly it shows that the H-P slope is positive which can be taken as an evidence that this relationship still holds in nanocrystalline Al - 7 wt. % Si alloys. A larger slope can be attributed to high density of dislocations in the ultra fine grains [34]. It is known that some models based on dislocation theory have been elaborated in order to interpret the Hall- Petch relationship. Among them, the pile-up model is mainly employed to deduce this phenomenological equation in metals and alloys. Since the free energy of grain boundaries is higher than that of grains, the grain boundaries may act as obstacles to dislocation slip. Therefore, the grain boundaries may strengthen the material. A refinement of grain size leads to more grain boundaries, and then provides more obstacles to dislocation pileup in the adjacent grains [37]. So, the refinement of grain size may cause an obvious enhancement of strength.

### CONCLUSION

- The effect of milling time on microstructure and hardness of nanocrystalline Al- 7 wt. % Si synthesized by ball milling technique were investigated by X-ray line broadening and Vicker hardness test, respectively.
- The average volume grain size, \( <D>_{\text{vol}} \) decreases from 89.85 to 64.15 69.26 nm over the range of studied milling time.
- The average dislocation density \( \rho \) was increased from 7.2 x10^{14} \text{m}^{-2} \) to 22.2 x10^{14} \text{m}^{-2} \) by increasing the milling time.
- The refinement of grain size may cause an obvious enhancement of strength.
- The positive values of Hall-Petch slope can be taken as evidence that this relationship still holds.

### REFERENCES


### Table I

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<th>&lt;D&gt;_{vol} (nm)</th>
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<th>μ</th>
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The effect of milling time on microstructure and microhardness parameters for nanocrystalline Al - 7 wt.% Si alloys.
Fig. 1. XRD of nanostructured Al-7wt.% Si alloys ball milled at different milling time (* Si; (Δ) Al and (Φ) Al Si)

Fig. 2. Lattice constants, a for Al-7wt.% Si alloys as a function of milling time.

Fig. 3. ln A(L) as a function of diffraction vector, k²C for nanostructured Al-7wt.% Si alloys ball milled for 48 hour.
Fig. 4. Size broadened term of Fourier coefficient as a function of Fourier length $L$ for nanostructured Al-7wt.% Si alloys ball milled for 48 hour.

Fig. 5. $M(L)/L^2$ as a function of $\ln L$ for nanostructured Al-7wt.% Si alloys ball milled for 48 hour.

Fig. 6. The dislocation density, $\rho$ with inversely, $<D>_{vol}$ for Nanostructured Al-7wt.% Si alloys ball milled at different milling time.
Fig. 7. Vickers micro-hardness (HV) of nanostructured Al-7 wt.% Si alloys ball milled for different milling time, versus the inverse root of volume grain size $<D>_{vol}$. 