Effect of Mechanical Alloying on the Dissolution of the Elemental Mn and Al-Mn Compound in Aluminum

Olga A. Yakovtseva 1, Nadezhda B. Emelina 1, Andrey G. Mochugovskiy 1, Andrey I. Bazlov 1,2, Alexey S. Prosviryakov 1 and Anastasia V. Mikhaylovskaya 1,*

1 Department of Physical Metallurgy of Non-Ferrous Metals, National University of Science and Technology “MISIS”, Leninskiy pr. 4, 119049 Moscow, Russia; yakovtseva.oa@misis.ru (O.A.Y.); emelina.nb@misis.ru (N.B.E.); mochugovskiy.ag@misis.ru (A.G.M.); bazlov@misis.ru (A.I.B.); prolex@misis.ru (A.S.P.)

2 The Research Laboratory for Mechanics of Advanced Bulk Nanomaterials for Innovative Engineering Applications, St. Petersburg State University, 7/9 Universitetskaya nab., 199034 St. Petersburg, Russia

* Correspondence: mihaylovskaya@misis.ru; Tel.: +7-(495)-638-44-72

Abstract: The grain boundary, solid solution, and precipitation strengthening mechanisms are important for controlling the mechanical properties of Al-based alloys. Due to severe plastic deformation, mechanical alloying refines grain structure to a nanoscale level which leads to a strong increase in solute content and the related strengthening effect of solute atoms and secondary-phase precipitates. This study analyzed the elemental Mn and Al6Mn phase dissolution in Al during high-energy ball milling. For this purpose, XRD data, microstructure, and hardness evolutions were compared for two Al—5.2 at% Mn alloys prepared by mechanical alloying using elemental Al and Mn powders and a pre-melted master alloy. In the two-phase master alloy, containing the Al solid solution and the Al6Mn phase, the strain accumulation, grain refinement, solid solution supersaturation, and milling-induced hardening effects were facilitated. Both elemental Mn and intermetallic compound were dissolved during mechanical alloying, and the maximum solute content was near 3.1 at% Mn. A fine crystalline size of ~25 nm and the maximum Mn solute content were observed after milling of elemental powders and the master alloy for 60 h and 20 h, respectively. The microhardness of ~3 GPa corresponded to a ~3.1% solute Mn content, and the microhardness increased to ~5 GPa after long-term milling due to precipitation strengthening effect of the secondary Al6Mn phase in the master alloy.

Keywords: aluminum alloys; solute content; mechanical alloying; microstructure; X-ray diffraction analysis; microhardness

1. Introduction

Due to their light weight and good mechanical properties, aluminum alloys are the most widely-used non-ferrous metallic materials. An increase in the mechanical strength at room and elevated temperatures is an issue for Al-based alloys and Al-matrix composites. The main strengthening mechanisms in these materials are precipitation strengthening, grain boundary strengthening, and solid solution strengthening. Severe plastic deformation can provide a high efficiency of these mechanisms due to a strong refinement of both Al matrix and precipitates [1]. Due to severe plastic deformation, the structure is in a state of high non-equilibrium, the solute content increases [2–6], and transformation to amorphous structures is possible [7–10].

Mechanical alloying produces nanocrystalline structures and provides for a high solubility of different alloying elements (Mn, Mg, Fe, Zr, etc.) in Al, even for low-soluble or immiscible elements, due to significant accumulated strain and a high density of crystallographic defects [11–14]. During high-energy ball milling, a high density of low-angle grain boundaries is formed which transform continuously to high-angle grain boundaries [15,16].
Thus, high-energy ball milling helps to obtain the nanograined Al matrix, a high solute content, and fine precipitates [17,18]. Milling parameters, ball material, balls-to-powder weight ratio, rotation speed, process control agent, and the alloys’ composition influence the mechanical alloying process and the accumulation of the lattice defects and microstructural evolution, i.e., solute content [19].

Aluminum–transition metal alloys (alloyed with Cr, Ni, Mo, Ti, Mn, V, Nb, etc.) processed by mechanical alloying demonstrate an ultra-high strength, corrosion resistance, and thermal stability [13,20–23]. Manganese in aluminum alloys is a promising alloying element for strength improvement due to the high thermal stability of the Mn-bearing precipitates, the good corrosion resistance of Al-Mn alloys, and the comparatively low cost of Mn. The equilibrium solubility of Mn in Al is limited by 0.62 at.% [24]. Meanwhile, the solute increases to 1–1.3 at.% Mn for continuous and electromagnetic casting [25–28], and up to 2–2.5 at.% for rapid solidification, like granular technologies and melt-spun ribbons [24,29]. An anomalously supersaturated solid solution with 7.5 at.% is observed for Al-Mn alloys prepared by electrodeposition from an ionic liquid [30]. For mechanical alloying of elemental Mn and Al powders, the maximum Mn solute content is 3.1 at.% and a nanograined structure with a high hardness is observed after milling for 200 h in a shaker mill [31]. Thus, long-term milling is required for nanostructure formation and increasing Mn solubility. A similar solute Mn and grain size are found in ternary Al-Mn-Cu alloys after milling for ~8 h due to the dissolution of intermetallic compounds in a planetary ball mill [32]. Pre-milling of the components in a planetary ball mill increases the solubility which can be up to ~4.0 at% Mn solute for Al-Mn-Cu alloys [33,34]. Regardless of the mill type and alloy compositions, the same processes occur during ball milling and after reaching the maximum solute Mn content of 3–4 at%, a further increase in the milling time leads to the precipitation of the Al₆Mn phase [31,35,36]. We assume that the dissolution of the phases of solidification origin can be more simple and rapid as compared with elemental powders due to a fine and homogeneous initial structure after solidification, intense strain hardening, and clear partially coherent/semi-coherent inter-phase boundaries. This study focuses on a comparison of grain refinement, dissolution kinetics of Mn in Al, and Mn solubility limits for two alloys processed by high-energy ball milling using elemental Al and Mn powders and pre-melted Al-Mn alloy (master alloy).

2. Materials and Methods

Assuming the possibility of a potentially higher solute Mn content in the binary alloy processed with high-energy ball milling in a planetary ball mill, the studied Mn content was chosen above the observed Mn solute limits, and Al-5.2 at% (10 wt%) Mn alloys were studied. Two types of mixtures providing Al-5.2 at% Mn were prepared: (Mode 1) a mixture of Al ASD-6 powder with a size of 0.5–5 µm and Mn flakes with a mean size of 1–3 mm and (Mode 2) a pre-melted alloy (master alloy). The alloys were prepared using 99.99 wt.% Al and 99.95 wt.% Mn. The master alloy was processed in an Interselt induction furnace (Interselt, Saint-Petersburg, Russia) at a melt temperature of ~1100 °C and then cast into a graphite mold with a solidification rate of ~20 K/s. For further high-energy ball milling, chips of the alloy were prepared using mechanical milling. Mechanical alloying was carried out in a Retsch PM400 high-energy planetary ball mill (VERDER company, Haan, Germany). Both powders and chips were treated in an argon atmosphere with grinding/break cycles of 5/5 min. The weight ratio of steel milling balls to the material being processed was 20:1. The rotation speed was 300 rpm. To prevent cold welding, a process control agent (~1 wt% of stearic acid) was added prior to milling. The time was varied in a range of 5 to 70 h.

The phase composition and solute content were studied with X-ray diffraction (XRD) in a D8 Discover diffractometer (Bruker Corporation, Billerica, MA, USA) in CuKα radiation. The lattice parameter was determined from X-ray diffraction patterns for Al lines with 2θ ≤ 140° by the extrapolation method. The size of the coherent scattering region (crystallite size) and microstrains were calculated via a Williamson–Hall method. For the studied
nanostructured alloys processed by high-energy ball milling, we consider the crystallite size to be similar to the grain size [31,32,37,38].

Differential thermal analysis (DTA) was performed using a Setaram Labsys DTA/DSC 1600 calorimeter and heating in the 20–680 °C range at a heating rate of 20 K/min. The granules’ weights were ~90 mg. For low-temperature background subtraction (below 660 °C), the DTA background line was received at the same heating rate for pre-annealed pure aluminum powder of a similar weight.

The size and microstructure of the granules after mechanical alloying were studied with a scanning electron microscope (SEM) TESCAN VEGA 3LMH (Tescan Brno s.r.o., Kohoutovice, Czech Republic) equipped with an X-MAX80 energy-dispersive X-ray spectrometer (EDS), Oxford Instruments. The samples were pressed with a self-hardening substance, mixed in a ratio of 1:1 with granules, to study the microstructure and microhardness of the granules. The samples were prepared by mechanical grinding with SiC papers of various dispersion and final polishing with a silica-based suspension (OP-S, Struers APS, Ballerup, Denmark) using a Struers LaboPoll-5 polishing machine (Struers APS, Ballerup, Denmark). The size of the granules was estimated from the mean diameter. The alloy composition was controlled after solidification and ball milling by SEM-EDS analyses at a low magnification of 300–500× for more than 15 microscopic areas. The deviation from the nominal composition for Mn was below 0.1 at%. The mean values were calculated by averaging more than 200 granules or particles. The error bars (confidence intervals) were calculated using standard deviation and the Student coefficient for a confidence probability of 0.95. The microhardness of the granules was measured by the Vickers method on a 402MVD microhardness tester (Wilson & Wolpert, Fort Worth, TX, USA) at a load of 25 g.

3. Results

The microstructure of the as-cast master alloy is shown in Figure 1a. After solidification, the alloy consisted of the dark Al-enriched matrix and bright Mn-enriched particles (see EDS elemental distribution maps in Figure 1b,c). The volume fraction of the particles was 0.33 ± 0.05. Due to a comparatively high cooling rate and a non-equilibrium solidification process, the Al-based solid solution contained more Mn than the equilibrium value of 0.62 at.%; according to SEM-EDS data, the mean Mn content in the Al-enriched areas was 1.5 ± 0.3 at% (~3.0 wt.%). Notably, this value did not take into account the overlapped signal from fine neighboring Mn-rich precipitates of the solidification origin phase.

Figure 1. (a) Microstructure of the as-cast master alloy with elemental distribution EDS maps for (b) Al and (c) Mn of the zoomed fragment of (a).

The evolution of the granular morphology and size distributions after mechanical alloying for the elemental powders and master alloy are shown in Figure 2. An increase in milling time led to an increase in the fraction of fine granules and a decrease in the mean granular size. A significant difference between the granular size of the alloys was revealed after a short milling time for 10 h (see Figure 2a,e and difference in solid and dash black lines in Figure 2h). For the alloy processed using elemental powders and a
high fraction of soft Al, the granular size varied from 60 to 300 µm, and the mean size was 170 ± 20 µm (Figure 2a). After the same milling time, the treatment of the hard master alloy produced uniformly distributed granules with a mean size of 9 ± 1 µm (Figure 2e). Milling for 20–40 h led to a mean granular size of (8–9) ± 1 µm for elemental powders (Figure 2b) and (5–6) ± 1 µm for the master alloy (Figure 2f). Increasing the milling time to 60–70 h provided a mean granular size of 4 ± 1 µm for the elemental powders (Figure 2d).

Figure 2. Granules morphology for the (a–d) elemental powders and (e–g) master alloy after milling for (a,e) 10 h, (b,f) 20 h, (c,g) 40 h, (d) 60 h; (h) is the granular size distributions for both alloys at the studied milling time range.

XRD analysis revealed peaks corresponding to Al and Mn for the samples processed using the elemental powders (Figure 3a), and the Al and Al₆Mn phases for the master alloy (Figure 3b) in milling time ranges of 5–60 and 10–40 h. With an increase in the milling time, the Al peaks’ wideness increased and their positions moved but the relative intensity of the Mn and Al₆Mn peaks decreased. After the milling of elemental powders for 70 h, the Al and Mn peak widths significantly increased and their peak intensity decreased; meanwhile, several new peaks corresponding to the Al₆Mn phase appeared (see zoom fragment in Figure 3c).

Figure 3. XRD patterns for the alloy processed using the (a,c,d) elemental powders and (b,e) master alloy after high-energy ball milling for different time; (c) is zoomed fragment of (a) at low 2θ angles; (d,e) demonstrate the changes of the Al (311) peak with milling time increase; the times of milling and phases are shown in graphs.
According to XRD peaks analysis, the crystallite size ($D$, coherent scattering region) of Al decreased from 40–43 nm to ~25 nm after long-term milling for 60 h for the elemental powders (Figure 4a). The same crystallite size was observed for the master alloy after milling for 20–40 h. The crystallite size of elemental Mn decreased from 14 nm at 5 h to 3.2 nm after 60 h of milling.

The microstrain component increased from 0.2 to 0.5%, and the corresponding dislocation density increased from $7 \times 10^{-10}$ to $2 \times 10^{-11}$ sm$^{-2}$ after long-term milling of the elemental powders (Figure 4b). A higher microstrain level and dislocation density were observed for the master alloy than for the elemental powders after the same milling time. The microstrain was 0.4–0.5% and the dislocation density was $(1–2) \times 10^{-11}$ after the milling of the master alloy for 10–20 h.

For the elemental powders, the evolution of the XRD data with milling time was analyzed in a time range of 5 to 60 h. The intensity of the Al reflections at large $2\theta$ significantly weakened after the milling of elemental powders for 70 h, and analyses of the crystallite size, lattice strain, and lattice parameter were impossible. The Al lattice parameter ($a$) (Figure 4c) decreased continuously from 0.4047 nm after 5 h to 0.4042 nm after 50 h and to 0.4037 nm after 60 h of milling, suggesting a ~2.9 at% Mn solute content in the elemental powders. For the as-cast state of the master alloy, the $a$ value corresponded to ~1.5 at% Mn in the Al-based solid solution that in agreement with the SEM-EDS data. For the master alloy, the minimum lattice parameter of 0.4036 nm was revealed after milling for 20 h that corresponded to 3.1 at% solute Mn content. A further increase in the milling time to 30–40 h led to an increase in the lattice parameter and a decrease in the solute content to 2.6 at% Mn. The error bars for the Al lattice parameter were <0.0001 nm.

Figure 5 shows the microstructure of the granules for two materials after processing. The microstructures were uniform and similar for fine and agglomerated granules of both
alloys studied. The SEM studies agreed with the XRD data and confirmed the phase composition of the alloys. For the elemental powders (Figure 5a,b,d), uniformly distributed bright-colored Mn-rich particles in the Al matrix were defined after milling for 5 and 20 h. The particles’ size varied in a range of 0.5–2.5 µm and their fraction was 7 ± 1%. With an increase in processing time to 60 h, the size of the Mn particles decreased to 0.2–0.5 µm, and the Mn-rich zones were clearly identified in the EDS elemental distribution map (Figure 5c,f). For the master alloy, the Mn distribution was nearly uniform but residual fine Mn-rich precipitates were also observed (Figure 5g–j). The rarely-distributed Fe particles incorporated from the milling balls were revealed in both alloys (see Figure 5b,g and element distribution map for Fe in Figure 5c,l). A low volume fraction of Fe particles of 0.1–0.2% was observed. The Fe content was ~0.35 wt% after milling for 20 h and ~0.6 wt% after milling for 60 h. These values are in agreement with the chemical analysis data for similarly treated aluminum-based alloys [32,33].

![Figure 5](image_url)

Figure 5. (a–c,g–i) The microstructure, (d,j,f) Mn and (e,k,l) Fe elemental distribution maps for the alloys processed by high-energy ball milling using (a–f) the elemental Al and Mn powders and (g–l) the Al-Mn master alloy.

The microhardness (Figure 4d) increased significantly with increasing milling time for both alloys; the master alloy demonstrated a higher hardness. The maximum values of ~360–400 HV and ~470–500 HV were reached after 50–60 h and 30–40 h of milling for the elemental powders and the master alloy, respectively.

DTA was carried out for the granules pre-milled for 20 and 60 h for the elemental powders and 20 and 40 h for the master alloy in order to compare the behavior of the alloys with different solute Mn contents (Figure 6). Two or three peaks were defined in the DTA curves of the milled granules. The first P1 exothermic peak was observed in a range of 100–120 °C to 180–240 °C for all of the studied regimes. The second P2 exothermic peak started at 300–380 °C. For the elemental powders, the P2 peak was not found after milling for 20 h, and a small exothermic P2 peak was observed at ~380 °C after milling for 60 h (Figure 6a). For the master alloy after 20 h milling, the P2 peak was revealed at ~320 °C.
An increase in the milling time to 40 h moved the peak position to a higher temperature of ~340 °C and the peak became weaker and broader. The last P3 endothermic peak was also observed for all the studied samples, the peak started at 608–610 °C and corresponded to the incipient melting point of the alloys (the melting of the eutectic consisted of the Al solid solution and Al₆Mn phase that agreed with the phase diagram).

Figure 6. (a) The heat-flow–temperature dependences for the granules milled for different times, and (b,c) XRD data for the granules pre-milled for 20 h and further heated to 420 °C for the alloys processed using (b) the elemental powders and (c) the master alloy.

The XRD data after pre-milling for 20 h and further heating to 420 °C with cooling to room temperature with a cooling rate of 50 K/min for the alloy processed using elemental powders and the master alloy are presented in Figure 6b,c, respectively. For the elemental powders, the Mn reflections were similar before and after annealing but the Al reflections moved to the left and Al₆Mn reflections appeared. For the master alloy granules (Figure 6c), the intensity of the Al₆Mn phase peaks increased strongly and the Al peaks moved significantly to the left, which suggested the solid solution decomposition and precipitation of the Al₆Mn phase. The Al lattice parameter 0.4048 ± 0.0001 nm after annealing was the same for both alloys that corresponded to ~0.5 at% Mn, and therefore the decomposition of the supersaturated Al-based solid solution was observed during heating to 420 °C and cooling to room temperature. After annealing, the crystallite size changed insignificantly but the microstrain decreased, $D = 39 \pm 2$ nm, $\varepsilon = 0.2\%$ and $D = 26 \pm 1$ nm, $\varepsilon = 0.2\%$ for the elemental powders and the master alloy, respectively. The dislocation density $\rho$ was $(8–9) \times 10^{10}$ sm$^{-2}$ for both modes in the annealed state. The hardness increased from 230 ± 20 to 250 ± 20 HV for the elemental powders and from 310 ± 15 to 333 ± 7 HV for the master alloy. Considering confidence deviations, the hardness insignificantly increased due to annealing.

4. Discussion
4.1. Dissolution and Precipitation Effects

The microstructure and lattice parameter evolution suggested the dissolution of the Al₆Mn phase at the beginning of milling up to 20 h, the decomposition of the Al-based solid solution, and the precipitation of the Mn-rich phases with a further increase in the time of mechanical alloying to 40 h. The master alloy behavior with Mn dissolution and further Al₆Mn precipitation was similar to that of the Al-Mn binary alloy processed with powders [31] and the Al-Mn-Cu-based alloys [32,33,39]. For the studied granules processed using elemental powders, the Mn dissolution occurred up to 60 h and the formation of the Al₆Mn phase was observed after 70 h of milling. For precipitation of the Al₆Mn phase during ball milling of the elemental powders in a shaker mill, longer-term treatment above 200 h was required [31]. The solute limit was ~3.1 at% Mn after milling of the master alloy for 20 h. The maximum milling time of 60 h provided a similar value of ~2.9 at% Mn for the alloy processed using elemental powder. These values are also in agreement with [31–33,39].
The difference in the dissolution kinetics for elemental Mn and the Al₆Mn phase could be the result of the differences in strain hardening, i.e., microstrain accumulation, and the corresponding refinement of the second phase and Al grains. Long-term milling was required for accumulating a high strain to refine the Mn particles and the soft Al matrix. For the as-cast master alloy, the Al matrix was harder owing to solute Mn atoms after non-equilibrium solidification. In addition, Al₆Mn particles, due to a high hardness and brittleness, were intensively refined and helped to increase the dislocation density and to refine the grain size of the Al solid solution. The high density of grain boundaries and the clear Al/Al₆Mn interfaces provided for a rapid dissolution of the intermetallic phase and an increase in the Mn solute content to the solubility limit. Meanwhile, the strain hardening effect and grain refinement are the most important. It is notable that for Cu bearing alloys, the Mn solute limit is revealed at a smaller milling time of about 5–7 h [32]. Copper is a strong solid solution strengthening element for Al [40] and it reasonably facilitates strain hardening and grain refinement during milling. The high solute content corresponded to the finest ~25 nm grains for both alloys. Thus, grain size is a critical parameter providing for an increased solubility of the alloying elements which is in agreement with [41].

Annealing of the milled granules led to recovery and recrystallization in the Al matrix and precipitation effects. We suggest that the low-temperature P1 peak in the DTA curves in a temperature range of ~100–240 °C corresponded to recovery and recrystallization in the severely deformed alloys in agreement with [22,42–44]. It is reasonable to suggest that the P2 peak corresponded to the decomposition of the solid solution and the precipitation of the secondary Mn-rich phases. The temperature of the P2 peak corresponded to the temperature range of Mn-rich phases’ precipitation in Al-Mn-based alloys [27,45–50]. For the elemental powders, the P2 peak was not observed after a short milling time of 20 h when the Mn solute content was low, ~0.9 at.%, and the P2 peak was found after 60 h of milling for the sample with ~2.9 at.% Mn solute. A lower peak temperature was observed during the heating of the master alloy sample pre-milled for 20 h with the maximum solute Mn content. The peak temperature increased and the peak height decreased in the sample milled for 40 h due to precipitation that started during mechanical alloying. Comparison of the XRD data of the milled and further annealed granules confirmed the presence of new reflections after annealing corresponding to the Al₆Mn phase that suggested the precipitation of this phase.

The hardness of the alloys strongly increased with an increase in the milling time. Grain sizes were similar to the other Al-based materials processed with mechanical alloying [51,52]. The grain size reduced to ~25 nm after milling for 60 h in the alloy processed with elemental powders and for 20–40 h in the master alloy. For the elemental powders, a maximum hardness of ~400 HV was observed after long-term treatment that increased the microstrain level and the dislocation density, refined the grains, and led to the maximum solubility in the studied time range. Fine 25 nm grains and the maximum 3.1 at% Mn solute were revealed after milling for 20 h and this time corresponded to a hardness of ~310 HV. The grain size, microstrains, and dislocation density were similar after milling of the master alloy for 20 h and 30–40 h, whereas long-term milling significantly increased the hardness values. According to the XRD data, milling for 30–40 h led to the decomposition of the Al solid solution and the precipitation of the secondary phase. Thus, fine secondary precipitates increased the hardness from ~310 to 500 HV. High-energy ball billing of the master Al-Mn alloy allowed us to decrease the milling time providing for the maximum Mn solubility and significantly increased the hardness of the alloy as compared to the elemental Al and Mn powders.

4.2. The Strengthening Mechanisms

Following Tabor’s ratio, \( \sigma_{YS} \) and the hardness (HV) are related through the equation 9.8 \( \times \) HV/\( \sigma_{YS} \) = 3 [53]. The yield strength can be theoretically estimated as a sum of contributions from various strengthening mechanisms (Equation (1)). The mechanisms are the lattice friction of pure Al (\( \sigma_0 \) ~20 MPa [54]), solid solution strengthening (\( \sigma_{SS} \),
grain boundary strengthening ($\sigma_{GB}$), dislocation strengthening ($\sigma_{dis}$), and precipitation strengthening. Precipitation strengthening can be provided by the precipitates’ shearing mechanism for fine and coherent precipitates \[55,56\] or the Orowan bypass mechanism ($\sigma_{Or}$) for non-shearable precipitates with a size above a critical value \[57,58\]. According to the rule of mixtures, the particles also contribute to the strength due to the difference between the hardness values of the particles and the matrix ($\sigma_{\text{ROM}}$) \[31\].

\[
\sigma_{YS} = \sigma_0 + \sigma_{SS} + \sigma_{GB} + \sigma_{dis} + \sigma_{Or} + \sigma_{\text{ROM}}
\]  

(1)

Solid solution strengthening can be calculated using Equation (2) \[59\].

\[
\sigma_{SS} = H \times C^\alpha,
\]  

(2)

where $\alpha$ and $H$ are constants and $C$ is the atomic concentration of solute atoms. According to \[59\], $\alpha$ is 1 and $H$ is 54.8 MPa/at.% for an Al-Mn solid solution with a 0.01 at.% Fe impurity.

The grain boundary strengthening mechanism is significant for the mechanically alloyed materials \[60\]. Grain boundary strengthening can be estimated using the Hall–Petch low (Equation (3)) \[1,61,62\].

\[
\sigma_{GB} = kd^{-1/2},
\]  

(3)

where $d$ is the grain size and $k = 0.06$ MPa·m$^{1/2}$ is the coefficient taken for nanocrystalline aluminum \[63,64\].

Dislocation strengthening can be calculated using Equation (4):

\[
\sigma_{dis} = M \alpha Gb \sqrt{\rho},
\]  

(4)

where $M \sim 3$ is the Taylor factor, $G = 26$ GPa is the shear modulus, $b = 0.286$ nm is the Burgers vector for Al, $\alpha \sim 0.24$ \[65\], and $\rho$ is the dislocation density.

Precipitation strengthening can be calculated using the Orowan equation (Equation (5)) \[57,58\].

\[
\sigma_{Or} = \frac{M \cdot 0.4 \cdot Gb}{\pi \sqrt{(1 - v)}} \frac{\ln\left(\frac{\overline{R}}{r_0}\right)}{\lambda}
\]  

(5)

where $\overline{R} = \frac{\pi R_S}{16}$ is the mean shear particle radius, $R_S$ is the particle radius, $r_0 = 1.5 b$, and $v = 0.345$ is Poisson’s ratio. The interparticle space $\lambda$ is calculated using Equation (6), where $f$ is the volume fraction of Mn-bearing dispersoids:

\[
\lambda = R_S \left(\sqrt{\frac{2\pi}{3f}} - \frac{\pi}{4}\right)
\]  

(6)

Strengthening provided by the difference in the hardness values of the particles and the matrix can be estimated through the rule of mixtures (Equation (7)) \[31\].

\[
\sigma_{\text{ROM}} = f \left(\frac{9.8H_p}{3} - \frac{9.8H_{Al}}{3}\right).
\]  

(7)

where $f$ is particle volume fraction, and $H_p$ and $H_{Al}$ are the hardness values of the particles and the Al-rich nanocrystalline matrix. The hardness of the Al₆Mn phase is 4900 MPa \[66\]. The hardness of nanocrystalline Mn and Al are 9000 MPa and 925 MPa, respectively \[31\].

4.2.1. The Strengthening Mechanisms for the Elemental Powders

For the alloy processed by elemental powders, the maximum solute content of 2.9 at.% Mn, the minimal grain size of 25 nm, and the maximum hardness of 409 HV or a yield strength of 1363 MPa were observed after milling for 60 h. For this Mn so-
lute content, $\sigma_{SS}$ was 160 MPa. The grain boundary strengthening $\sigma_{GB}$ was ~380 MPa. The dislocation density was $2 \times 10^{11}$ cm$^{-2}$ and the corresponding contribution $\sigma_{dis}$ was ~250 MPa. The hardness of Mn is much higher than that of Al. According to the rule of mixtures, an undissolved fraction of 0.03 Mn ($\sigma_{ROM}$) contributed about 80 MPa to the total strength. Considering the calculated contributions, the $\sigma_{Or}$ can be extracted from Equation (1) as follows.

$$\sigma_{Or} = \sigma_{YS} - \sigma_0 - \sigma_{SS} - \sigma_D - \sigma_{GB} - \sigma_{ROM}$$ (8)

Considering all strengthening mechanisms, the Orowan strengthening should provide ~470 MPa. For the experimentally determined values of 0.7 at% Mn in Al and a Mn particles’ fraction of 0.07 after 5 h milling, the Mn solute content was 2.9 at% and the mass fraction of undissolved Mn particles decreased to 0.03 after 60 h. Thus, the Orowan strengthening contribution should correspond to a precipitate size of ~5 nm.

4.2.2. The Strengthening Mechanisms for the Master Alloy

The maximum concentration of 3.1 at.% Mn in the solid solution was observed after mechanical alloying for 20 h. The total hardness of the master alloy milled for 20 h was 305 HV, and therefore $\sigma_{YS}$ was ~1000 MPa. Following Equation (2), $\sigma_{SS}$ was ~170 MPa. The mean grain size and the dislocation density after milling for 20 h were 25 nm and $10^{11}$ cm$^{-2}$, respectively. Considering the 5.2 at% Mn content in the alloy, the concentration of Mn in the insoluble particles was 2.1 at% (4.2 wt%). Taking into account that the Al$_6$Mn phase density is 3.32 g/cm$^3$, the volume fraction of Al$_6$Mn particles after milling for 20 h was ~0.14. Thus, according to Equations (3), (4), (7), and (8) the $\sigma_{GB}$, $\sigma_{dis}$, $\sigma_{ROM}$, and $\sigma_{Or}$ parameters were ~380 MPa, 170 MPa, 190 MPa, and 70 MPa, respectively. Considering the residual fraction of the particles, the $\sigma_{Or}$ value corresponded to an average particle size of ~200 nm that was in agreement with [31]. The key strengthening mechanism was grain boundary strengthening which provided the maximum solute content after milling for 20 h.

An increase in the milling time to 40 h increased the hardness to 501 HV, which corresponded to $\sigma_{YS}$~1633 MPa. The mean grain size changed insignificantly to ~27 nm and the grain boundary strengthening contribution was also high ~365 MPa. For a 2.6 at.% Mn solute content and 2.6 at.% in the Al$_6$Mn phase, the precipitates’ fraction was 0.17, and thus $\sigma_{SS}$ was 143 MPa, and $\sigma_{ROM}$ was 235 MPa. Considering the dislocation density of $1.7 \times 10^{11}$ cm$^{-2}$ after 40 h of milling $\sigma_{dis}$ was 220 MPa, the Orowan strengthening mechanism should provide ~655 MPa that corresponds to a mean particle size of ~12 nm. It is reasonable to assume that the fine secondary precipitates that formed during the low-temperature solid state reaction in a milling time range of 20 to 40 h should be about several nanometers in size. These secondary precipitates contribute to a significant decrease in the mean particle size and improve the strengthening effect as compared to the particles of solidification origin phases for the master alloy processed for 20 h.

It should be noted that other unconsidered strengthening mechanisms or precipitation of hard X-ray-amorphous phases (with the size and fraction below the critical ones for XRD) can also influence the hardness after long-term milling. The presented calculation of the Orowan mechanism strengthening considered dislocation movement as the predominant deformation mechanism for the nanostructure [67]. If the accumulation of dislocations in nanograins during plastic deformation is impossible [68], the deformation mechanisms can be controlled by grain boundary activity, grain boundary precipitates, grain boundary dislocations interactions, grain boundary sliding, and grain rotation, as well as deformation twinning [69–71]. For this case, the fine precipitates may effectively pin grain boundaries and dislocation emission and inhibit grains movement, thus increasing the strengthening effect.
5. Summary

The microstructure characteristics and hardness evolution of two Al-5.2 at% Mn alloys processed by mechanical alloying using elemental Al and Mn powders and a pre-melted master alloy were compared. Both elemental Mn and the thermodynamically stable Al₆Mn phase were dissolved in Al during mechanical alloying and the maximum solute Mn content was ~3.1 at% after 20 h of milling for the master alloy and ~2.9 at% after 60 h of milling for the alloy processed using the elemental powders. An important result of this study is that the milling of the master alloy significantly reduced the processing time required to form a supersaturated solid solution of Mn in Al and also significantly increased the hardness of the granules. After mechanical alloying for 40 h, the hardness of the master alloy was two-fold that of the alloy processed using elemental powder. For the Al-Mn master alloy, the maximum hardness of ~5 GPa was provided due to the grain boundary strengthening of the nanocrystalline matrix with a 2.6 at% solute Mn content and nanoscale secondary precipitates of the Al₆Mn phase.

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