Nanocrystallization of Al Powder by Cryomilling Process†

Mohammad Hossein Enayati
1 Department of Materials Engineering, Isfahan University of Technology, Iran

Abstract
Al5083 powder was subjected to ball milling in liquid nitrogen for 8 h using an attrition ball milling. The evolution of morphology of powder particles and the refinement of grain size were studied by scanning and transmission electron microscopies. The results showed that during cryomilling the morphology of powder particles changed from spherical to equiaxed shape. Additionally, the size of powder particles increased from ~10 μm to ~20 μm with narrower distribution. Simultaneously the cryomilling was associated with a significant reduction of grain size so that the final product after 8 h of cryomilling had a nanocrystalline microstructure (~25 nm) with well-developed high angle grain boundaries. These features were discussed in terms of severe plastic deformation, cold-welding and fracturing of powder particles which occur simultaneously during cryomilling process.

Keywords: cryomilling, aluminium, Al5083, nanocrystalline powder

1. Introduction

Nanocrystalline materials are generally known as those materials that have a crystallite size less than 100 nm. This upper limit of 100 nm is based on the fact that most properties (mechanical/physical/chemical) of materials start to change significantly at this point. Although there are lots of experimental results showing that the change in properties can occur in crystallite size much smaller or in some cases larger than 100 nm. In conventional coarse-grained polycrystals, with a typical grain size of 10 μm, the fraction of boundaries is very small. In contrast if the grain size reduces to nanocrystalline state (grain size < 10 nm) a high fraction (1018–1021 cm–3) of material is boundaries. As a result, grain boundaries have significant contribution in physical and mechanical properties of nanocrystalline materials. Nanocrystallization leads to the hardness and strength enhancement and improvement of diffusivity, solid solubility, sintering ability and magnetism.

Vapor deposition, plasma processing, gas-condensation, chemical precipitation and crystallization from the amorphous phase are well established processing routes for obtaining nanocrystalline materials. However, it is well known that mechanical milling (MM) and mechanical alloying (MA) as solid synthesis routes can also be applied for production of a nanocrystalline as well as nano-composite powders with high uniformity (Fogagnolo J.B. et al., 2004). Comparison of different preparation methods in terms of cost and productivity demonstrates that MM/MA is the most cost effective route capable of producing nanocrystalline materials in large quantity. It is worth mentioning that powder particles prepared by MA/MM are rarely monocrystals. Instead, MA/MM powders have micrometer dimensions with interior nanometer microstructure. The structure of each particle can be described as a poly-nanocrystalline. The final powder produced by MA/MM can be subsequently either consolidated by standard powder metallurgy techniques into bulk materials with desirable properties or deposited on surfaces of engineering parts using various thermal spraying methods.

It has been proved that grain refinement of powders in MM/MA to the nanometre size is governed by the plastic deformation induced during milling. In general, the grain size decreases continuously with milling time until a minimum (saturation) size is approached (Enayati M.H., 2015; Hellstern E. et al., 1989). Further refinement seems to be difficult to achieve for a fixed set of experimental conditions. Transmission electron microscopy (TEM) observations have revealed that nanocrystallization starts with development of shear bands and dislocations pile-ups at the early stages of milling (Eckert J. et al., 1992; Hellstern E. et al., 1989). With increasing milling time more dislocations are created in the grains leading to a dislocation cell structure and then low-angle boundaries. This stage is finally followed by development of a fully nanocrystal-
The higher the $T_m$ or the bulk modulus, $B$, of the respective metals. The higher the $T_m$ or $B$, the smaller the $d_{\text{min}}$ is obtained. However, no clear inverse correlation between the minimum grain size and melting temperature was observed for BCC metals Cr, Fe, Nb, W as well as for HCP metals Hf, Zr, Co, Ru. Koch C.C. (1989) observed that only the lower melting temperature FCC metals ($\leq T_m$ for Pd) exhibit an inverse dependence of $d_{\text{min}}$ on $T_m$.

The dependence of minimum grain size versus melting temperature has been discussed with respect to the competing rates of creating dislocations due to work hardening and recovery phenomena which scale with the melting point, $T_m$, or the bulk modulus, $B$, of the respective metals. Thus, the smaller the $d_{\text{min}}$, the higher the $T_m$ or $B$, the smaller the $d_{\text{min}}$ is obtained.

Experiments have revealed that the minimum grain size for a given material is a constant value independent of milling conditions. In fact, the minimum grain size is determined by intrinsic properties of materials such as melting temperature, crystal structure and deformation behavior. The milling conditions can only affect the rate at which the grains refine and approach the minimum size. Eckert et al. (1992) observed that the minimum grain size, $d_{\text{min}}$, in a series of FCC metals including Al, Cu, Ni, Pd, Rh and Ir scales inversely with the melting point, $T_m$, or the bulk modulus, $B$, of the respective metals. However, no clear inverse correlation between the minimum grain size and melting temperature was observed for BCC metals Cr, Fe, Nb, W as well as for HCP metals Hf, Zr, Co, Ru. Koch C.C. (1989) observed that only the lower melting temperature FCC metals ($\leq T_m$ for Pd) exhibit an inverse dependence of $d_{\text{min}}$ on $T_m$.

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Table 1 lists the chemical composition of as-received and recovered Al5083.

| Physical Properties | Value |
|---------------------|-------|
| Density             | 2.65 g/cm³ |
| Melting Point       | 843 K   |
| Electrical Resistivity | $0.058 \times 10^{-6}$ Ω·m |
| Thermal Conductivity | 121 W/m·K |
| Thermal Expansion   | $25 \times 10^{-6}$/K |

| Mechanical Properties | CW↑ | CW↓ |
|-----------------------|-----|-----|
| Modulus of Elasticity (GPa) | —   | 72  |
| Proof Stress 0.2 % (MPa)      | 240 | 145 |
| Tensile Strength (MPa)         | 345 | 300 |
| Shear Strength (MPa)           | 190 | 175 |
| Elongation A5 (%)              | 13  | 17  |
| Hardness Vickers (HV)          | 95  | 70  |

**Table 1** Some physical and mechanical properties of Al5083 alloy

Cryomilling process includes several advantages over room temperature ball milling. A benefit of cryomilling is that the rate of diffusional process like annihilation of dislocation is extremely limited at cryogenic temperature. As discussed earlier, under this condition the grain refines with a much higher rate. Hence the milling time required to attain a certain grain size is significantly reduced. Shorter milling time in case of cryomilling implies that a large quantity of powder can be processed in large-scale low-energy ball mills within a reasonable milling time.

The present research was aimed to study the process of nanocrystallization in Al5083 alloy during cryomilling. Synthesis of nanocrystalline structure in different aluminum alloys has been widely investigated but the nanocrystallization in cryomilling condition have been rarely reported. Al5083 alloy is a non-heat treatable aluminum alloy. As a result the strengthening of Al5083 is essentially restricted to cold working/work hardening. However, the strength of Al5083 may be further enhanced by scaling the grains size down to the nano range. Because of excellent combination of engineering properties (see Table 1) such as strength, weld ability and corrosion resistance, Al5083 has different applications specifically in chemical industries and marine environments.

### 2. Materials and methods

Gas atomized Al5083 powder was used as starting materials. Table 2 lists the chemical composition of as-received...
Al5083. The compositions of samples were determined using an energy dispersive X-ray spectrometer (EDX). The main alloying elements in this alloy was found to be Mg with traces of Cr, Zn, Ti, Fe, Cu, Si and Mn. To prevent oxidation or hydration, the powder was stored in vacuum chamber before cryomilling.

Cryomilling was performed in an attrition ball mill. Fig. 1 shows a schematic configuration of milling apparatus.

Fig. 1 Schematic representation of cryomilling apparatus.

This type of mill comprises a static cylindrical vessel with a rotating impeller with which a rather large quantity of powders (several kg) can be processed making it potentially suitable for commercial exploitation. The powder to be milled was placed in a stationary tank with balls and liquid nitrogen. This mixture was then stirred by the shaft with arms, rotating at a high speed of about 180 rpm. Table 3 shows the cryomilling parameters used in this study.

The milling media including milling tank, shaft, impeller and balls were martensitic stainless steel 440C (Fe-18Cr-1.2C-1Mn-1Si) with a hardness of 60 HRC. A problem with ball milling process is the adhesion of powder particles on milling surfaces reducing the powder yield. The sticking of powders on milling surfaces is caused by severe cold welding of powder. Extensive cold welding also results agglomeration of powder particles which leads to the coarse powder particles. These phenomena are more serious in the processing of ductile materials like aluminum. The adhesion of powders can often be overcome by adding a surface-active agent to the powder mixture in order to inhibit the cold welding process. In this study 0.2 weight percent stearic acid-as a surfactant- was added to the powder mixture. Stearic acid is a waxy solid with chemical formula of C_{17}H_{35}CO₂H.

The morphology of powder particles was analyzed in a Philips XL30 FEG scanning electron microscope (SEM) operating at 10 kV. The powder particles size was determined on SEM micrographs using ImageJ software. Powder samples were fixed in small quantities on a sample holder by Ag conductive paint. At least 50 separate particles were chosen for the measurement of powder particle size.

A CM20 transmission electron microscope (TEM) operating at 200 kV was used for observation and characterization of the internal structure of cryomilled Al5083 powders. A small amount of powder sample was dispersed in methanol using ultrasonication for ten minutes. The obtained suspension of particles was lifted on a carbon-coated Cu grid (400 mesh) by dipping the grid in the suspension gently and removing horizontally. The grid was then dried in air for several hours. The resulting specimens showed some thin areas suitable for TEM observation.

### 3. Results and discussions

Fig. 2 shows SEM images of as-received Al5083 powder particles with different magnifications. As seen Al5083 particles were spherical in shape with a wide size distribution. The spherical morphology of

![Fig. 2 SEM images of as-received Al5083 powder particles with different magnifications.](image-url)
as-received powder indicates that the powder was prepared by gas atomization process in which a stream of molten metal is mechanically disintegrated by a jet of high-pressure gas. Under this situation the cooling rate of the molten droplets is sufficiently slow for surface tension forces to spheroidize them before solidification occurs. The surface image of a particle is presented in Fig. 2c indicating a typical solidification morphology.

The powder particles size was analyzed on SEM using ImageJ software. The result showed that as-received Al5083 powder particles had a size distribution of 3–15 μm with a mean size of ~10 μm.

Changes in particles morphology and microstructure during ball milling of ductile metal powders are produced by two simultaneous processes; cold welding and fracturing. During ball milling clusters of particles are trapped between colliding balls and undergo a high level of impact. If the impact stresses are sufficient, the powder particles plastically deform and flatten (see Fig. 3b). As the powder particles are pressed together their surface area increases and the surface oxide films rupture, consequently exposing clean underlying metal. When these fresh surfaces of particles come in contact a metal bond is formed. After a period of milling, particles deform to the extent that cracks initiate, propagate and ultimately fracture the particles. In first stage the cold welding process dominates and as a result the powder particle size continuously increases. This stage can be also termed the agglomeration stage.

The progressive increase in hardness value during the first stage due to the work hardening leads to a decrease
in the ductility of powder particles and therefore, an increased tendency for particle fracture. Thereby, the first stage is followed by the fragmentation stage. During the fragmentation stage the fracturing of particles occurs more readily than cold welding and as a result the powder particle size decreases. The extent of these two events is determined by the mechanical properties of the elemental powders, such as ductility, yield stress and hardness, as well as the magnitude of the impact provided by colliding balls. The last stage is a steady-state stage in which there is a balance between the frequencies of cold welding and fracturing processes so that the average particle size remains unchanged. As illustrated in the following paragraph these three stages are associated with microstructural changes.

The TEM images presented in Fig. 4 shows bright field (BF) images and selected area diffraction patterns (SADP) of several Al5083 powder particles after cryomilling for 8 h showing a well-developed nanocrystalline structure.

![TEM images](image)

**Fig. 4** Bright field (BF) images and selected area diffraction patterns (SADP) of several Al5083 powder particles after cryomilling for 8 h showing a well-developed nanocrystalline structure.

(e.g. oxide or nitride compounds).  
Similar to conventional room-temperature ball milling the transformation of coarse-grained structure to a nanosized scale during cryomilling includes several successive stages; gradual increasing of dislocation density due to plastic deformation of powder particles, formation of sub-boundaries by annihilation and recovery processes and eventually development of high-angle boundaries by the absorption of more dislocations into the boundaries.

For those cryomilling processes in which the powders are mixed with liquid N\(_2\), the reaction of constituents with N\(_2\) must be considered. This reaction seems to proceed to a great extent during ball milling as plastic deformation; flattening and fracturing of powder particles repeatedly produce fresh, clean and highly reactive surfaces. The powder-N\(_2\) reaction can be more serious in case of reactive elements such as Al and Ti. However, TEM results in Fig. 4 do not support this prediction. During cryomilling the nitrogen picked up was found to be 0.11 wt%. Nitrogen dissolved interstitially in Al lattice forming a supersaturated solid solution. It should be noted that because of low temperature, formation of nitrogen-containing dispersoids such as AlN are kinetically improbable, although there is a large driving force for the formation of such compounds (e.g. \(\Delta G^{AlN} = -287 \text{ kJ mole}^{-1}\)).

However, subsequent heating upon powder consolidation of cryomilled Al5083 can lead to the formation of...
Various secondary phases including AlN and Al₂O₃. The presence of these precipitates was confirmed in previous studies by atom probe field-ion microscopy (FIM) and high-resolution transmission electron microscopy (HR-TEM) observations but the volume fraction of precipitates was not determined (Zhou F. et al., 2001). Furthermore, the X-ray diffractometry of cryomilled powder after heat treatment showed no traces of secondary phases suggesting that the amount of the dispersoids are virtually very small < 1 vol% (Zhou F. et al., 2001). It is worth noting that the dispersion particles formed during cryomilling acquired nanoscale size ranging from 1–30 nm, with majority of 3–10 nm. The average spacing between the dispersoids was measured to be less than 10 nm. These dispersions were found to be incoherent in nature, highly stable at high temperature and insoluble in matrix. The presence of these finely dispersed particles can play a critical role in retarding grain growth in the nanocrystalline materials through the so-called Zener mechanism even though their volume fraction is low. Furthermore, they could effectively obstruct dislocation motion and therefore reduce the minimum grain size.

4. Conclusions

Similar to conventional room temperature ball milling process cryomilling of aluminum powder led to the nanocrystallization. The ultimate grain size appeared to be similar to that reported for conventional ball milling (25 nm) although the rate of nanocrystallization was found to be much faster. Furthermore, in cryomilling the cold-welding process increased the powder particle size with more uniform morphology compared to as-received powder.

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Author’s short biography

Mohammad Hossein Enayati

M. H. Enayati (PhD, CEng) is a full Professor of materials science at Isfahan University of Technology and Fellow of Institute of Materials, Minerals and Mining (FIMMM), UK. Prof. Enayati’s research focuses on the nanostructured and amorphous materials, mechanical alloying and synthesis of advanced materials for thermal spray coating. He has authored several books and numerous articles in well recognized international journals in his field, and has received research funding from a wide variety of agencies. His research has been recognized with numerous awards, most recently from the Iran Nanotechnology Initiative Council and Iranian Nanotechnology Society.