Effect of diamantane on the thermal stability of cryomilled aluminum alloy

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Abstract

The thermal stability behavior of Al-5083 cryomilled nanocrystalline powders stabilized by diamantane nanoparticles was studied in comparison with the alloy without diamantane. Nanocrystalline Al 5083 powders were produced by mechanical milling in a liquid nitrogen medium. The results revealed that Al 5083 with diamantane showed higher thermal stability than the cryomilled alloy without diamantane in the temperature limit from 473 °K to 773 °K (0.56 to $0.91T_m$) for various annealing times from 0.5 h to 48 h. In this regard, calculations showed that while the grain size was still in the nano scale in the presence of diamantane, it was in the ultrafine range (> 150 nm) in the absence of diamantane. The above finding was qualitatively explained in terms of Zener's concept. Copyright © 2019 VBRI Press.

Keywords: Cryomilling, diamantane, grain boundaries, nanocrystalline materials, thermal stability.

Introduction

The average grain size of Nano crystalline (nc) materials should be equal or less than 100 nm. Due to that characteristic, junction lines, grain boundaries, and nodes have significant effect that can affect the characteristics in higher level than in conventional materials [**1**].

Notable among top-down processes that have been used for producing nanocrystalline materials is cryomilling [**2**]. Cryomilling process can be up scaled to a large-scale production. From many years this process has got considerable attention due to its adaptability. The outcome at the end of the milling is a flaky powder instead of sphere, which also requires consolidation. The procedures for consolidation are accomplished at elevated temperatures, causing a higher grain growth passing the nc-regime. In this way the nc-grains tend to be largely unstable according to prediction of Gibbs-Thomson equation [**3**]. By using low temperatures in other processes, high porosity of the product will occur. Applications of the highest developments are also need specific materials that require the stability of the microstructure.

It is preferred to improve the thermal stability of Aluminum alloys higher than that gained through the dispersion of second-phase particles, such as Al_2O_3, aluminum nitrite and aluminum carbide particles, which occur during the cryomilling process. A different way of going at that is to disperse nano particle through the grain boundaries and the grain itself in the process of cryomilling. In a recent work [**4**], the investigation of thermal stability in Aluminum with 0.5 weight % diamantane was done. The annealing at different temperatures till 500 °C for ten hours, the average grain size for cryomilled nanocrystalline aluminum powders containing diamantane was much smaller than 100 nm.

The production of thermally stable nanocrystalline Aluminum powder by the addition of diamantane nano particles during cryomilling has made a huge discovery in the nano material industry. In this work we concluded to examine the grain size of 5083 aluminum alloy powder after milling and annealing at elevated temperature would or would not be in the nano scale range. This examination is useful as a first step in the process of consolidating the alloy.

Experimental

Materials

The target Al alloy, Al 5083 (4.4 wt% Mg, 0.7 wt% Mn, 0.15 wt% Cr, balance Al), was selected for two main reasons. First, this alloy has been used in several applications (rail cars and vehicles body). Second, data on its microstructural and mechanical characterization as a result of cryomilling are available [**5, 6**].

In this study the Diamantane diamondoids was come by Chevron Texaco Technology Ventures–Molecular Diamond Technologies (Richmond, California). Diamantane are saturated, polycyclic cage – like hydrocarbon. The homologous series of diamondoids have the general formula C_{4n+6} H_{4n+12}, so diamantane consisting of 14 C atoms [**7**]. As mentioned elsewhere [**4**], the selection of diamantane was chosen for many reasons. For most, the size of the diamantane molecule is less than 2 nm in diameter so it comfortably fit onto the grain boundaries of nano crystalline aluminum alloy. Next, the structure of diamantane is strong, rigid and highly stable. Last, it can be easily isolated from different hydrocarbons in crude oils. It is possible to approximately estimate the amount of diamantane that should be added to Al 5083 Al by adopting the following equation [**8**], which gives the grain size, d, and the grain boundary thickness δ, are controlling the volume fraction of the grain boundaries.

$$f_{gb} = 1 - \left(\frac{d-\delta}{d} \right)$$

A value of $f_{gb} = 0.05$ was estimated from Equation by substituting an average grain size of 30 nm for powders of cryomilled Al and its alloys and a grain boundary thickness of about 0.5 nm [**2**]. The quantity of diamantane needed to account for about half of this volume fraction (0.025) have to be enough to have a meaningful effect on grain growth assuming that the diamantane is primarily dispersed along the grain boundaries due to the consequence of cryomilling. This amount was also deemed sufficiently low to avoid forming a successive layer of diamantane at the boundaries that may be harmful. To meet these requirements, the composition of diamantane is given by:

$C_{dia} = f_{gb} * \rho_{dia} / 2\rho_{Al5083}$ where ρ_{dia} and ρ_{Al5083} are the densities of diamantane and 5083 Aluminum ally, respectively.

Taking $\rho_{dia} = 1.21$ g/cm^3 and $\rho_{Al5083} = 2.67$ g/cm^3, a reasonable addition of diamantane for an intensive dispersion of individual cages on the boundaries was estimated to be 0.55% by weight. Accordingly, a 0.5 wt. % addition of diamantane was used in the present study.

Materials synthesis

Nanocrystalline Al 5083 powders were produced by mechanical milling in a liquid nitrogen medium. The as-received commercial Al 5083 powder of a particle size of 10 – 12 micrometer was milled with 0.5 % diamantane (first run), without diamantane (second run) in an grinder with a stainless steel ball at charge of 180 r/min. The milling medium was liquid nitrogen. Throughout the milling process that was 8 hours, liquid nitrogen was put on exactly into the mill to be shore of complete immersion of the milling system. According to published data [**2, 4, 5**], cryomilling Al and its alloys for 8 h produces the minimum grain size. The temperature in the vial was from -180 °C to -190 °C [**4**]. The stainless-steel balls of 6.4 mm in diameter were used as the grinding media and the ball-to-powder weight ratio was 30 to 1. Before the beginning of the cryomilling we add approximately 0.2 weight percent of stearic acid [$C_{17}H_{35}$ - COOH] to the powders which acts as process control agent preventing the powder adhesion to the milling tools.

Characterization

The investigation of the microstructure were done using the techniques of X-ray diffraction (XRD) and transmission electron microscopy (TEM), Both XRD and TEM were used to provide grain size measurements as a function of time. While XRD yields the values of the average grain size, TEM has the advantage of providing the distribution of grain size, from which the average grain size can be estimated. In addition, TEM and SEM were utilized to check the development of the nanostructure during cryomilling. Details of steps involved in applying the above techniques are given elsewhere [**4-6**].

Results and discussion

Particle size of the 5083 Al alloy

There are significant changes in the morphology of Aluminum 5083 with 0.5 % diamantane and the as received powder, the shapes of the powder was changed after cryomilling to polygonal flaky instead of sphere in the as received powder and the average particle size of the as received particle is 9.5 micrometer and the average particle size of Aluminum 5083 with 0.5 diamantane is 11 micrometer. **(Fig. 1)** show the shapes of the particles.

(Fig. 1a) show SEM of the as received particle and **(Fig. 1b)** show SEM of after cryomilling with 0.5 % diamantane for 8 hours.

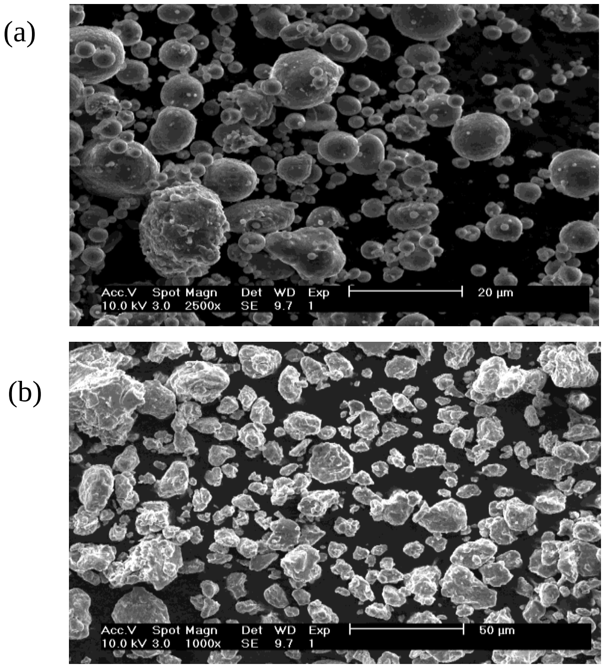

Fig. 1. (a) The as received Al 5083 powder, 1(b) Al 5083 with 0.5 % diamantane after cryomilling.

Thermal stability of the powder of 5083 Al alloy

Typical examples for X-ray Spectra are given in **(Fig. 2)** Consideration of a large number for these spectra and using the integral breadth (IB) method for estimating the grain size shows the following trends [**9**]:

Comparing the XRD spectra of the cryomilled Al 5083 alloy with 0.5 % diamantane and the XRD of as received Aluminum 5083 powder shows that there is no shift in the 5 peaks of Aluminum as a result of cryomilling and the addition of diamantane.

Also, comparing the XRD spectra of the cryomilled Al 5083 with 0.5% diamantane and without diamantane shows that there is a very small shift in the position of the peak or peak broadening in the XRD spectra of cryomilled Al 5083 with diamantane and cryomilled Al 5083 without diamantane after cryomilling for 8 h.

Therefore the diamantane that added produces no lattice strain in the 5083 Al matrix. This finding is in agreement with that reported for cryomilled Al with and without diamantine [**4**].

For Al 5083 without diamantane and with diamantane after cryomilling for h, calculations indicate that the average grain size is 23 nm and 18 nm, respectively.

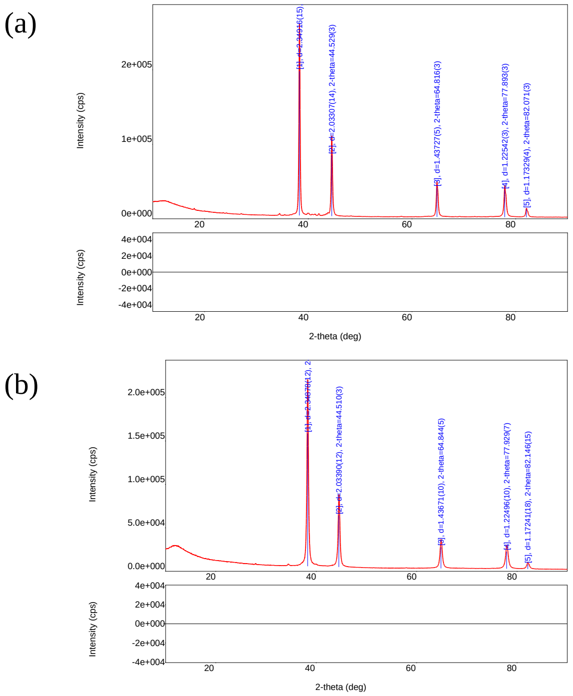

Fig. 2. (a) Al 5083 after milling without diamantane, 2. (b) Al 5083 after milling with diamantane.

The investigation of the grain growth behavior, isothermal annealing was done at different temperatures from 473 °K to 773 °K (0.56 to 0.91T_m) for various annealing times from 0.5 h to 48 h. The average grain size values were measured from numerous representative XRD spectra similar to those given in **(Fig. 2)** using the IB method [**9**]. Examination of these values for 5083 Al alloy with 0.5 weight % diamantane, which are plotted as a function of time and temperature in **(Fig. 3)** reveals the following findings:

(a) The rate of grain growth is rapid during the initial period of annealing, and then later decreases with increasing time. This comparatively early growth may correspond to recovery of some boundaries, a phenomenon that facilitates the reduction of stored energy by the removal or rearrangement of dislocations [**2, 4**].

(b) The increase in grain size with temperature is relatively small at low temperature.

(c) The growth rate decreases with increasing exposure time at a given temperature. Significant growth is only observed at temperatures greater than 623 °K.

(d) Even at the highest temperatures the grain size remained well below 100 nm.

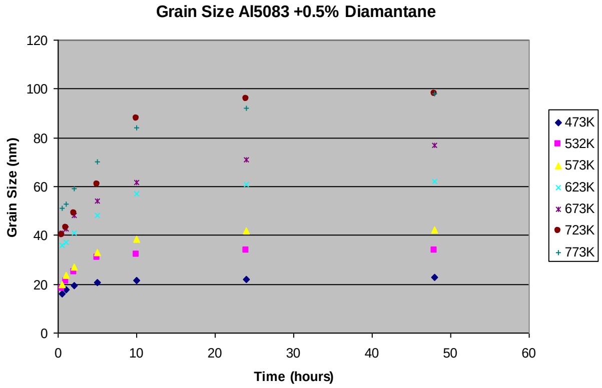

Fig. 3. Grain size versus time of the annealing for cryomilled 5083 Al with 0.5 % Diamantane.

Fig. 4 shows a representative TEM micrograph. **(Fig. 4a)** bright field along with a selected area diffraction pattern (SAD) of 5083 Al with 0.5 diamantane after cryomilling, **(Fig. 4b)** The selected area diffraction pattern displays a ring arrangement, showing that the individual grains are primarily separated by high-angle grain boundaries and have a random orientation with neighboring grains.

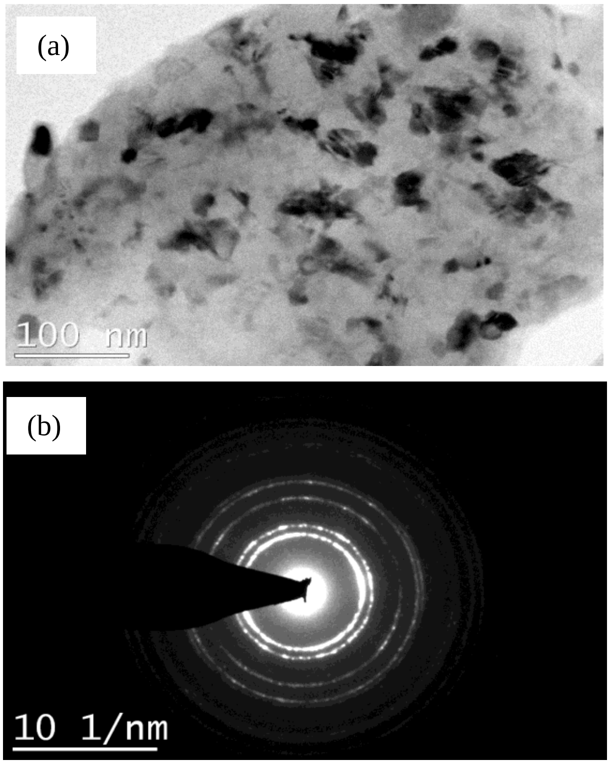

Fig. 4. (a) Bright-field image, 4(b) Selected diffraction patterns.

Typical examples for TEM micrographs that show a comparison in terms of grain size between Al 5083 after cryomilling without diamantane and with 0.5 % diamantane at 200 ºC (473°K) and 10 h are shown respectively in **(Fig. 5a)** and **(Fig. 5b)**.

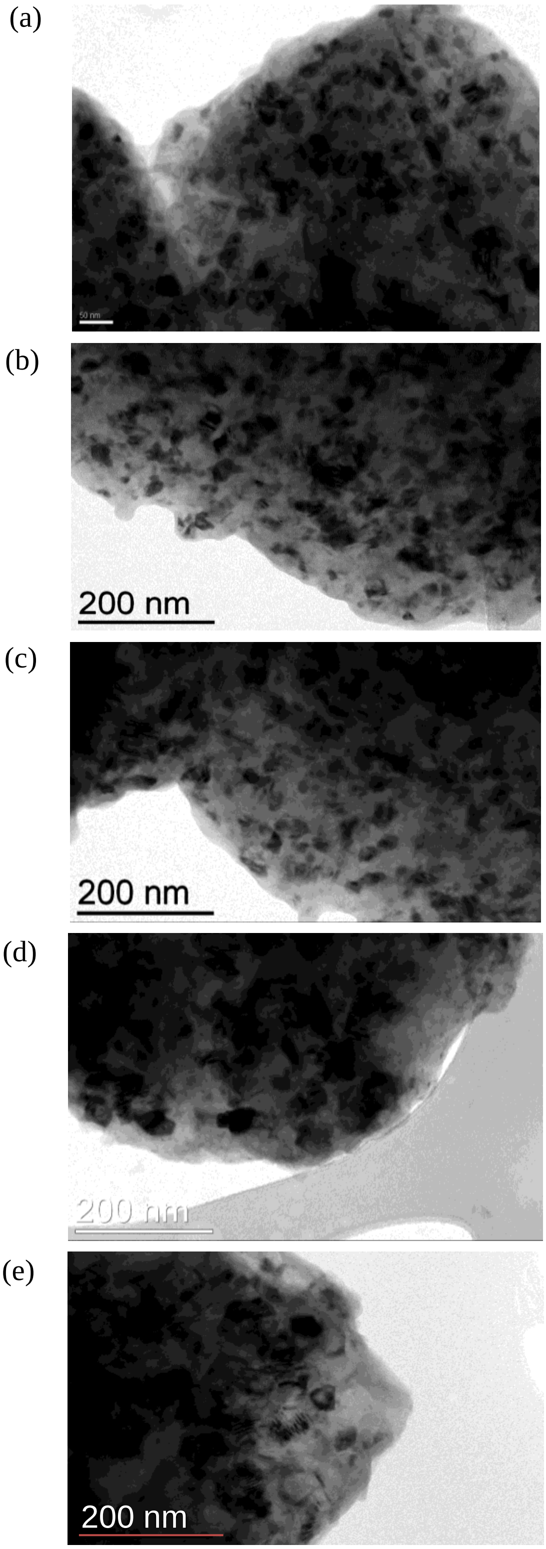

Fig. 5. (a) As milled, (b) 200°C (473 K) at 10 h without diamantane, (c) 200°C (473 °K) at 10h with 0.5 % diamantane, (d) 400°C (673 °K) at 10hr with 0.5 % diamantane, (e) 400°C (673° K) at 48hr with 0.5 % diamantane.

Calculations based on a large number of representative TEM micrographs reveal that while the grain size is still in the nano scale in the presence of diamantane, it is in the ultrafine range (> 150 nm) in the absence of diamantane, i.e., the grain growth of Al 5083 with 0.5 % diamantane is less than without diamantane. For example, the average grain size for Al 5083 with 0.5 % diamantane at 500 ºC (773 °K) for 48 h is about 97nm, a value that falls in the nanocrystalline range, but for Al 5083 without diamantane is 205 nm that is in ultra-fine-grained range.

(Fig. 6) provides a comparison between the averages of grain size as measured by XRD and those inferred from the TEM histograms as a function of annealing temperature (ºC). An examination of the figure reveals that while the measurements by XRD and TEM are similar in terms of trend and the results of the minimum grain size after milling. XRD, d = 20 nm and for TEM, d = 23 nm), there are two significant differences:

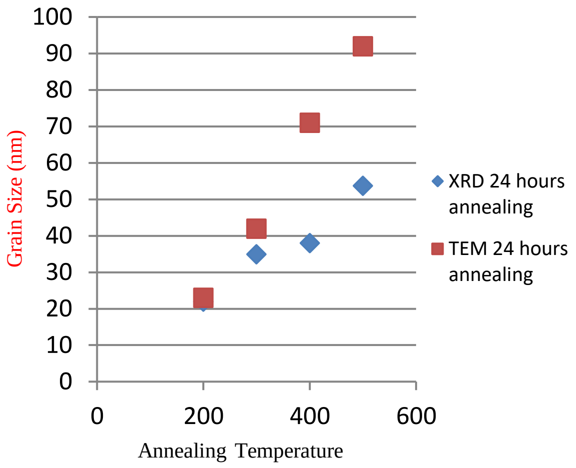

Fig. 6. The grain size measurement determined from TEM and XRD measurements 24 h annealing.

(a) At temperatures > 300 ºC (673 °K), there is a discrepancy from the values of d conclude from TEM and those estimated from XRD peaks.

(b) The extent of such a discrepancy increases with increasing temperature. The reason for the discrepancy is that the technique of XRD cannot provide accurate measurements for grains sizes whose values > 100 nm [**10**] and as a result, using this technique would guide to an undervaluing of the average grain size.

Table 1 compares the average grain size after Thermal stability in bulk ultrafine-grained (UFG) 5083 Al that was processed by gas atomization followed by cryomilling, consolidation, and extrusion, from previous work [**6**] that exhibited an average grain size of 305 nm, was investigated in the temperature range of 473 to 673 °K, where, *Tm* is the melting temperature of the material for different annealing times.

Table 1. Compares the average grain size of 5038 Al alloy with and without diamantane.

Temperature	Annealing Time (H)	With Diamantane (nm)	Without Diamantane (nm)
200 °C (473 °K)	10	21	305
200 °C (473 °K)	48	24	314
400 °C (673 °K)	10	66	680
400 °C (673 °K)	48	79	780

The previous research on cryomilled nc-Al powders had revealed the presence of second-phase dispersion of Aluminum oxide and Aluminum carbide particles [**5, 6**].

It is generally accepted that the obtained modified phase particles in a polycrystalline material can constrain grain growth by pinning their boundaries. In this regard, pinning arises from two processes:

(a) Accumulation of particles at boundaries. Incoherent particles exhibit the tendency to accumulate at the boundaries since they reduce their areas and hence the energy of the system.

(b) Boundary motion. In this process, the boundary motion is impeded since its migration requires the creation of more boundaries, where particles previously resided, which in turn generally leads to an energy increase.

The above two processes form the origin of the concept initially proposed by Zener in a communication to Smith [**11**]. Their treatment showed that the pinning force between a single particle and a boundary could be given by:

$$F = \pi\gamma(r)$$

where, γ is the grain boundary energy and r is the particle average radius. For the case in which many particles interact with the boundary [**11**], Eq. (2a) can be written in the following form:

$$\mathrm{F} = (3/2)\gamma(f/r)$$

where, f is the volume fraction of pinning particles. The particle spacing, λ, is related to the volume fraction, f, by the following equation [**12**]:

$$\lambda = \sqrt{l/f}$$

where, l and t are the length and thickness of the particle, respectively.

Through the years, the concept recommended by Zener [**11**] was adapted to regard various effects involving the following: (a) the geometry of particle-grain boundary interaction [**13**], (b) the mutual action of coherent particles with boundaries [**14**], and (c) a random-particle distribution [**15**].

Conclusions

(a) Aluminum 5083 powders were cryomilled with 0.5 weight percentage diamantane for 8 hours bringing out mechanically alloyed powders with an average grain size of about 22 nm.

(b) Al 5083 with diamantane showed higher thermal stability than the alloy that cryomilled without diamantane in the temperature limit from 473 °K to 773 °K (0.56 to $0.91T_m$) for various annealing times from 0.5 h to 48 h. Calculations based on a large number of representative TEM micrographs reveal that while the grain size is still in the nano scale in the presence of diamantane, it is in the ultrafine range (> 150 nm) in the absence of diamantane.

(c) The values of grain size measured by TEM and XRD are similar in terms of trend and the amount of the smallest grain size after milling (for XRD, d = 20 nm and for TEM, d = 23 nm). However, at temperatures > 300 ºC (673 K), there is a discrepancy between the values of d inferred from TEM and those estimated from XRD peaks; and the extent of such a discrepancy increases with increasing temperature. The reason for the discrepancy is that the technique of XRD cannot provide accurate measurements for grains sizes whose values > 100 nm. As a result, using this technique would lead to an underestimation of the average grain size.

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