The fracture strength of cryomilled 99.7 Al nano-powders consolidated by high frequency induction sintering

Ehab A El-Danaf, Muneer Baig, Abdulhakim A Almajid, Mahmoud S Soliman

aMechanical Engineering Department, College of Engineering, King Saud University, Riyadh, Saudi Arabia

bAdvanced Manufacturing Institute, King Saud University, Riyadh, Saudi Arabia

E-mail : edanaf@ksu.edu.sa

Abstract. Mechanical Attrition of metallic powders induces severe plastic deformation and consequently reduces the average grain size. Powders of 99.7 Al (45µm particle size), cryomilled for 7 hrs having a crystal size of ~ 20 nm, were consolidated by high frequency induction sintering under a constant pressure of 50 MPa and at two temperatures of 500 and 550 °C for two sintering dwell times of 1 and 3 minutes at a constant heating rate of 400 °C/min. The bright field TEM image and X-ray line broadening technique, for the cryomilled powders, were used to measure the crystallite size. Simple compression at an initial strain rate of 10^-4 s^-1 was conducted at room temperature, 373 and 473 K, and the yield strength was documented and correlated with the sintering parameters. The as-received 99.7 Al powders-consolidated using one of the sintering parameters was used as a reference material to compare the mechanical properties. Hardness, density and crystal size of the consolidated sample, that gave the highest yield and fracture strength, were measured.

1. Introduction
During mechanical milling, metal powder particles are subjected to severe plastic deformation from collision with milling balls [1,2]. Consequently plastic deformation at high strain rates occurs within the particles and the average grain size is reduced. The process leading to grain size reduction includes three basic stages; first the deformation is localized into shear bands consisting of high – density dislocations. Second, at a certain strain level, these dislocations annihilate and recombine as small angle grain boundaries. Finally, the small angle grain boundaries change their orientation under further deformation and randomly oriented nano-meter scale grains are formed. This mechanism was further elaborated upon by Xun et al. [3] and these steps were associated with three phenomena happening at specific structural scales: a macroscopic level (level of individual powders), a mesoscopic level (level of individual small fragments), and a microscopic level (level of individual grains). At the macroscopic level, the formation of a nanocrystalline (nc ) structure is accounted for by the repeated strain fatigue fracturing and cold welding caused by cycling impacting loading in random directions. Because the low milling temperature leads to transgranular fracture, the fracturing and cold welding are likely to refine grains by forming new grains at the welding interface from the fragments of the original coarse grains. At the mesoscopic level, individual fragments are refined through a bimodal process that is reflected in the following: (1) the plastic damage is surmised to occur via impacts from the balls; and (2) the impact energy stored in the form of shear bands consisting of an array of dislocations
with higher density. At the microscopic level, the starting grain is large in size (on the order
of microns) and almost dislocation free. With increasing interior strain, the dislocation
density increases gradually. At a certain strain level, these dislocations will form sub-
boundaries by aligning, annihilating, and recombining with each other. With further
deformation, the low angle sub-boundaries are changed to high-angle boundaries (true
boundaries) by the absorption of more dislocations into the boundaries or accompanying
grain rotation. Finally, the grain size reaches a given constant size. Once this size is reached,
further refinement ceases. It is reported [1] that the milling time to reach the final stage was
significantly shorter for cryomilling than that for conventional milling performed at ambient
temperature, which was attributed to the suppression of the recovery effect at cryogenic
temperature.

The aim of this work is to study the cryomilling of a commercial purity aluminum powder at
various milling times, and evaluate the crystal size achieved. A novel sintering technique was
employed, namely high frequency induction sintering (HFIS) that is characterized by high
heating rate. The sintering parameters, in present investigation, were the sintering
temperatures of 500 and 550 °C and sintering dwell times of 1 and 3 minutes. This sintering
technique was selected to examine the possibility of minimizing grain growth due to short
heating/dwelling time.

2. Experimental Procedures

The cryomilling is conducted in a 1 gallon 304 stainless steel tank in an attritor procured
from Union Process, USA. A ratio of 1:30 powder to stainless steel ball weight ratio was used.
In addition, 0.2 wt% stearic acid was added to the powders in the vial at the beginning, as a
process control agent to minimize cold welding of particles. The impeller is rotated at 150
rpm and then the balls are charged followed by the powders and stearic acid, then the valve
for liquid nitrogen flow is opened for maintaining a liquid nitrogen medium in the milling
vial during the whole attrition period. The rotation of the shaft is then increased to 250 rpm.
After the intended milling time of 2, 5 and 7 hours, the powder is collected in slurry form
from a valve underneath the milling vial. The slurry is then dried in a drying vacuum oven at
a temperature of 250°C and a vacuum level of ~ 10⁻⁴ torr for 3 hours. The powders after
drying is checked for crystal size by the X –diffraction using X-ray line broadening technique
proposed by Scherrer [4, 5].

In addition, the 7 hours as-cryomilled powder was examined using transmission electron
microscopy (TEM). TEM sample preparation consisted of suspending the nanostructured
powders in methanol, agitating the solution by hand, and submersing a Cu TEM grid into the
methanol where the powders adhered to it. Micrographs of the powders were produced using
a JEOL JEM 7600F transmission electron microscope operated at 200 kV. Average grain size
was determined directly from the TEM micrographs by measuring the diameters of 300
grains using Image J image analysis software (National Institute of Health). Bright field TEM
images were used for this grain size determination following the procedures of Zhou et al. [6].
The dried powders were consolidated by HFIS in graphite dies under a constant pressure of
50 MPa in a vacuum chamber of 10⁻³ torr. The induced current frequency was approximately
50 kHz based on previous study [7]. Details of compaction process are described elsewhere
[7]. The sintering conditions were varied among sintering temperatures (500 and 550 °C) and
sintering times (1 and 3 min.) with a constant heating rate of 400 °C/min for all samples. The
sintering condition is presented, for example as 500 °C/400 °C/1 min., which gives sintering
temperature, heating rate and sintering time, respectively.
The mechanical behavior of consolidated samples was investigated by compression testing at room temperature, 100 and 200°C using an Instron universal testing machine (model 3385) at a cross-head speed corresponding to initial strain rate of $10^{-4}$ s$^{-1}$. High pressure grease was used to nearly isolate the effect of friction from the output data. The deformed specimens showed very little barreling (less than 1%). The density and hardness of the consolidated sample, that gave the highest compression strength values, were measured by means of Archimedes' principle and Vickers Microhardness test machine at a load of 200 g and a dwell time of 15 sec, respectively.

### 3. Results and Discussion

Fig. 1(a) presents the (111) peak for powders cryomilled for 7 h demonstrating the broadening of the peak for which the small crystallite size is contributing. Fig. 1 (b) presents the effect of milling time on the crystallite size of the milled powders as calculated by the Scherrer formula after correcting for instrumental broadening using a strain free silicon single crystal. It is seen that after 7 h of cryomilling, the crystal size is reduced to around 23 nm. A TEM bright-field image of Al powder cryomilled for 7 h, as presented in Fig. 1 (c), indicates nanosized grains (<100 nm). A histogram of the grain size distribution, based on the analysis of 300 grains, for this specimen, is presented in Fig. 1 (d) which illustrates the frequency vs. grain size range. The average grain size for TEM measurements is 19 nm with standard deviation of 6 nm. This value is essentially similar to that based on XRD measurements.

After drying the powders, the particles were charged into a graphite die 10 mm in diameter between two fitting punches. The die was placed in a high frequency induction heat sintering press and pressed to 50 MPa. At that point heating was commenced with a specified heating rate (400 °C/min). The pressure was maintained throughout the whole test via a LVDT. Fig. 2 present the true stress – strain response under simple compression for all the consolidated samples at room temperature. The results show that the sample consolidated with condition of 500 °C/400 °C/min)/3 min gave the highest flow stress levels, in terms of yield and fracture strength values. Also, it is noted the higher plastic deformation capability for the samples consolidated at 3 minutes compared to the 1 minute consolidated samples, which indicates the better level of densification for higher sintering dwell time for both temperatures.

Fig. 3 shows the true stress –strain response in simple compression for the cryomilled and consolidated sample that gave the highest flow stress levels compared to as-received powders consolidated under the same consolidating conditions of 500-400-3. It can be concluded that the yield strength has increased by about a factor of 8.

The stress strain response at 100 and 200 °C was evaluated in simple compression to characterize the thermal stability of the consolidated samples. It should be mentioned that the samples were heated to the respective temperature between ceramic anvils with a thermocouple attached to the sample surface and soaked for 15 minutes before compression was commenced.
Fig. 1 (a) The (111) XRD peak for the powders cryomilled for 7 hours and the reference sample, (b) Variation of crystal size for the powders with milling time based on XRD measurements, (c) TEM bright-field image of Al powder cryomilled for 7 h, (d) grain size distributions for the TEM micrograph.
Fig. 2 True stress-strain curves under compression for consolidated samples tested at room temperature at various sintering conditions.

Fig. 3 The true stress–strain curves under compression for the cryomilled and consolidated sample that gave the highest flow stress levels (500/400/3) as compared to as-received consolidated powders.

Fig. 4 (a, b) shows the true stress-strain response for the samples consolidated at 500°C and for the two sintering times of 1 and 3 min., respectively, for two testing temperatures of 100
and 200°C. A strain rate jump test was conducted on all samples for both testing temperatures from a strain rate of $10^{-4}$ to $10^{-2}$ s$^{-1}$, to evaluate the effect of sintering conditions and testing temperature on the strain rate sensitivity, $m$.

The flow behaviour of deformed materials at constant strain is usually described by Eq. 1 [8]:

$$\sigma = C \dot{\varepsilon}^m$$  \hspace{1cm} (1)

Where $\sigma$ is the flow stress, $\dot{\varepsilon}$ is the strain rate and $C$ is a constant, which depends on the experimental conditions like temperature and grain size. The value of $m$ is determined from the following relation [8]:

$$m = \ln \left( \frac{\sigma_2}{\sigma_1} \right) / \ln \left( \frac{\dot{\varepsilon}_2}{\dot{\varepsilon}_1} \right)$$  \hspace{1cm} (2)

To determine $m$ a strain rate jump test from strain rate of $\dot{\varepsilon}_1$ to $\dot{\varepsilon}_2$ is applied on the deformed specimen and the corresponding $\sigma_1$ and $\sigma_2$ are calculated, respectively. The high value of $m$ in fine grained materials correlates with the good ductility of these materials despite high strength and low strain hardening coefficient.
Fig. 4 strain rate jump tests from $10^{-4}$ to $10^{-2}$ s$^{-1}$ for all samples at both temperatures to determine m values.

Fig. 5 shows the variation of strain rate sensitivity parameter for the four sintering conditions for both testing temperatures of 100 and 200 °C. Three findings can be concluded; first, the higher testing temperature of 200 °C always displayed a relatively greater strain rate sensitivity. Second, the sample consolidated at 500-400-3 which gave the highest flow stress levels gave the highest strain rate sensitivity of 0.03. Third, all values of strain rate sensitivity was relatively low due to the presence of porosity in consolidated samples along with the possibility of second phase inclusions resulting from the cryomilling process. The increase in testing temperature ($\leq 0.5 T_m$) can result in grain size coarsening that promotes strain hardening (reduces dynamic recovery), as observed in the true stress – strain response shown in Fig. 4. This behavior is consistent with that observed in submicron-grained aluminum [9-11].

The yield strength for each consolidation condition as a function of temperature (25, 100 and 200 °C) are depicted from the true stress –strain response and plotted in Fig. 6. It is seen that for all three consolidation parameters of 500-400-3, 550-400-1 and 550-400-3 the strength was reduced to about 210 MPa at 200 °C, which is still much higher than the yield strength of the as-received powder consolidated sample which gave a yield strength of about 45 MPa at room temperature.

The density, hardness and crystal size of the consolidated sample that gave the highest flow stress levels are 2.54 g/cm$^3$ (94% of full density), HVN 115 and 97 nm, respectively. The level of densification of 94% of full density for this consolidation route is rather acceptable. The crystal size was barely kept below 100 nm. The Vickers microhardness is about 115 Hv which is related to the yield strength of 320 MPa from the compression of the consolidated bulk sample, by factor of about 2.8.
Fig. 5 $m$ values as determined from strain rate jump tests

Fig. 6 variation of yield strength with temperature
4. Conclusions

A 45 µm particle size 99.7% Al powder was cryomilled for 7 hours to give a crystal size of about 23 nm. Consolidating the cryomilled and dried powders via high frequency induction sintering facility with sintering conditions of 500 °C/ 400 (°C/min)/ 3 minutes gave a yield strength of 320 MPa and true plastic strain at fracture of 2.8% in simple compression. The crystal size after consolidation has increased to about 97 nm barely below the 100nm upper limit for bulk nanocrystalline materials. That particular sample gave strength level that is eight times higher than the bulk consolidated sample from the as received powders. The yield strength for that sample dropped to 210 MPa at 473 K due to the temperature effect.

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