

The Effects of the Different Approaches of Measuring Size of Nanocrystalline Materials on their Thermodynamic Properties

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Abstract

The intrinsic influence of the bonding energy on thermodynamic properties of nanocrystalline materials deformed by accumulative roll bonding (ARB) invested to study the increase in energy on property. A unique method was proposed to compute the thermal properties of nanomaterials size variants during ARB. The interrelation between thermodynamic and mechanical properties during ARB was analyzed based on different approaches of measuring size. The following facts were theoretically derived. It was shown that as time increases during grain refinement the energy variation in the material increases. It was also shown that the evolution of size and increase in energy in the material during grain refinement is similar to the Hall Petch and Reverse Hall Petch relationship during ARB.

Keywords: Increase in energy, Size variants, nanocrystalline material, thermodynamic and yield stress.

I. INTRODUCTION

Nanomaterials have novel thermal and mechanical properties which are completely different from conventional materials [1-8]. There are several theoretical and experimental research investigations on nanomaterials the size-dependent mechanical and thermal properties of nanomaterials after accumulative bonding experimentation [1-8]. Few of this research models revealed the increase in temperature, and it impact in sizes and properties [1-8]. Most commonly the results focused on the revealing trend of the thermodynamic and mechanical properties of their parameters which must deals with decreasing grain size of nanoparticles and nanostructure and their impact on thermodynamic and mechanical properties specifically the material internal energy during grain refinement or entropy effect on property [1-9]. These analyses mostly focused on parameters that consist of melting entropy and also the melting point of materials [6-15], most.

importantly the Debye temperature [10,16,17] and the cohesive energy models [6,18-23], also the diffusion activation energy volume [24,25], the amplitude of the thermal vibration process [26,27], the thermal expansion coefficient of the materials [28-30], specific heat content of the materials [31,32], Young's modulus of nanomaterials [33-36], and mass density [37,38] are also involved in the derived models of

thermodynamics properties. Most of these models are derived based on the general analysis of high surface-to-volume ratio of nanomaterials. Nanomaterials are generally noted for their high surface to volume ratio which affect all the properties of nanomaterials [1-15]. It is noted that the proportionality of nanoparticle at the surface of a material is not negligible and therefore nanoparticles at the exterior of a particle surfaces possess higher energies than nanoparticle at the interior of a particle surface. For the past decades in research much volume of data has been established in both theoretical and experimental study. In most of the obtained data in theoretical and experimental analysis it is shown that the mechanism of the size effect is not clear because of the variation of these experimental results [1-10]. This has resulted to the current controversies in nanomaterials mechanical properties when comparing different obtained results [1-10]. Some advanced derived models based on the classical thermodynamics and modern molecular dynamics simulation still revealed more controversies. More so most derived models focus on limited parameters and give different explanations without looking at the increase in energy during grain refinement and it impact in yield stress and sizes [1-11]. This has resulted to lack of fundamental understanding of the mechanism of size effects on nanomaterials increase in energy during ARB as more study only focused on energy and internal energy. In the current paper the varying effect of measuring size is investigated in increase in energy and the effect on sizes and property are tested during ARB process. This will help in understanding grain growth phenomena as grain growth is greatly affected by increase in energy during grain refinement.

II. THEORETICAL MODEL

Figure 1 is a physical schematic used to derived the relevant model for the description of the energy change of a nanoparticle given by (Xiaohua Yu and Zhaolin Zhan) which is modified in this work to show the increase in energy in mobility of atoms and it impact on thermal and mechanical property. From Fig.1 it can be assumed from a perfect crystal based on Figure 1A that there are no defects in the schematic and all the atoms are located at their normal equilibrium lattice positions before deformation takes place due to ARB process. In the same system as shown in Fig.1, we assumed as given by (Xiaohua Yu and Zhaolin Zhan) that

the atomic radius is r_0 and the density of the crystal is ρ_0 when the system is in equilibrium. Taking the assumption to a nanoscale mechanic or nanoscale system it can be assumed that at nanoscale the shape is closely spherical with a given radius R_0 taken out of a perfect crystal shown in Fig.1B. Therefore, as bond cleavage of the atoms surface takes place in the system, the outside atoms of the particle moved from their equilibrium positions leading to compression of the particle that was initially in equilibrium. As this happen the external radius decreases to R . The average gyration radius is r and the average density is ρ_R . From fundamental principle, the mass is conserve and the mass of the sphere in the spherical system is equal to the mass outside the particle. This can be defined as a ratio given by equation (1) and equation (2) from Fig. 1.

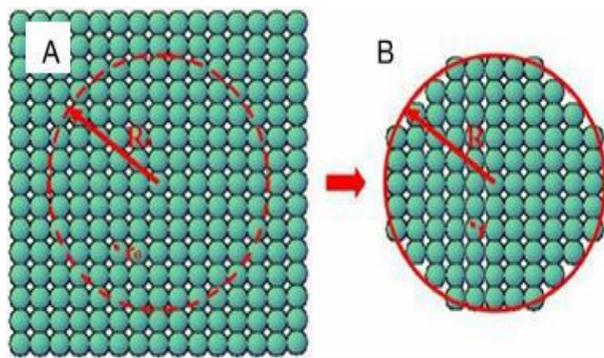


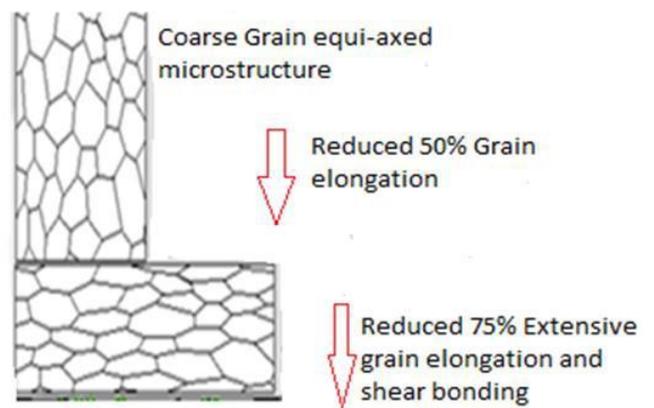
Fig.1 A perfect crystal (A) and a nanoparticle taken out of it (B). (A) All the atoms are located at their equilibrium lattice positions. The atomic radius is r_0 and the density is ρ_0 . (B) The particle radius is compressed from R_0 to R , the average gyration radius reduces to r , and the average density increases to ρ_R . (Image courtesy from Xiaohua Yu and Zhaolin Zhan)

$$\frac{R_0^3}{r_0^3} = \frac{R^3}{r^3} = \frac{N}{n} \quad (1)$$

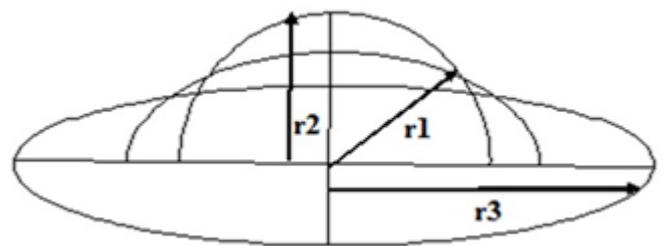
Equation (1) give the relationship between the overall number of atoms in the particle N and atomic packing factor n . The relationship between density and average density is given by equation (2)

$$\frac{\rho_0}{\rho_g} = \left(\frac{R}{R_0}\right)^3 - \left(\frac{r}{r_0}\right)^3 \quad (2)$$

The relationship between overall volume of atom in the cell and volume of atom in the cell define n is given as $n = \dots$. However the from empirical analysis, the particle radius which is compressed from R_0 to R and the average gyration radius reduces to r can be related to microscopy analysis during grain deformation by ARB process which is a process which affect the mobility of atoms (nanoparticle). Therefore Fig.2 (a) revealed the microscopy analysis and Fig. 2 (b) revealed the schematic of an atom or nanoparticle being analyzed in different approaches of measuring size of nanoparticle during grain refinement.



(a)



(b)

Figure 2 deformed materials after ARB cycles (b) Schematic of elongated grains due to deformation in 3-D grain.

The particle radius is compressed from R_0 to R . In modelling this is related to 3-D analysis which is a real-life problem and as such the initial grain size is r_0 before compression takes place. When compression takes place in 3-D, based on microscopic observations and the schematic shown in Fig.2 (a) and (b), it was observed that the semi major axis length r_1 and major axis length r_3 initially increased and then decreased since grain breakages took place in these directions. As a result of this repeated lengthening and grain breakage processes the effective lengths of r_1 and r_3 decreased during grain refinement.

It was also observed during grain refinement that the equivalent axis radius r and semi minor axis length r_2 decrease continuously. It was further observed that r_2 and r_3 were evolved as proportions or fractions of r and r_1 respectively. The following models are derived based on stochastic consideration of grain size evolution. Since r_1 increased and instantaneously decreased after breakage, the evolution of r_1 during grain refinement can be represented as;

$$dr_1 = M \left(\frac{1}{r_{c1}} - \frac{1}{r_1} \right) dt + r_1^{\frac{1}{2}} D dW(t) - Z r_1 V_1 d(t) \quad (3)$$

where $\langle \dots \rangle =$ the expected value, r_{c1} =local critical grain size, Z and D are Constants, $dW(t)$ =change of the Wiener process, $V_1 = \tau_1 r_1^2$ defines rate of grain breakage, $M = M_0 \left(1 + \frac{CD}{r_1} \right)$ is

Grain Boundary (GB) mobility function, $CD = 4(Hm)(h_0)/((k)(T))$, $T_m = T \{\ln(m_0/m)\}$ and $M_0 = M_0 \exp\{-T_m(\ln)/T\}$ = initial grain boundary mobility constant, $dW(t)$ is of Wiener process and $dN(t)$ is the number of coalescence events within an infinitesimal time interval. Since r_3 decreases as a fraction or proportion of r_1 during grain refinement, r_3 can be represented.

$$dr_3 = Ratio_1(dr_1) \quad (4)$$

Since equivalent radius r decreases continuously during grain refinement, r can be represented by

$$dr = -Odt + IdW(t) \quad (5)$$

where O and I are constants. For r_2 that decreases as a fraction of r during grain refinement, r_2 can be represented.

$$dr_2 = Ratio_2(dr) \quad (6)$$

Based on the observation during grain elongation and change in grain size variants during grain refinement. the energy of the outside nanoparticle would increase by ΔW . This change will include the change in surface energy W_1 being induced by bond of cleavage of the surface atoms and W_2 being the lattice distorted energy induced during compression due to surface tension outside the particle due to the compressive force from the rollers during grain

refinement. The derived expression is given as

$$\Delta W = W_1 + W_2 \quad (7)$$

From the principle of thermodynamic, the surface energy of a particle out of a surface is equivalent to the increase of the Gibbs free energy. in fact this implies that surface energy outside the particle can be computed by taking the surface tension being the applied force on the material and the area of surface outside the particle being a closely spherical surface of the particle given as

$$W_1 = \rho \frac{4}{3} \pi R^3 = N \sigma \frac{4}{3} r_0^2 \frac{r_0 \rho_0}{R \rho_R n} \quad (8)$$

The lattice distortion energy W_2 is the change in area of one atom given as

$$W_1 = N \sigma \frac{4}{3} \pi r_0^3 \left(1 - \left(\frac{r}{r_0}\right)^3\right) \quad (9)$$

The overall bonding energy W_0 can be given as

$$W_0 = \sigma \frac{4}{3} \pi r_0^3 \quad (10)$$

The expression for the variation of energy can be given as

$$\frac{\Delta W}{W_0} = \frac{\Delta E}{E_0} \quad (11)$$

The Zhao (Zhao et al., 2006:472) model gives the relationship between yield stress and grain size that depicts HPR to RHPR given as

$$\sigma(r) = \sigma'_0 + A \left(r^{-\frac{1}{2}}\right) - B(r^{-1}) - C \left(r^{-\frac{3}{2}}\right) \quad (12)$$

where $\sigma'_0 = \sigma_0 + K_t$ is bulk yield stress, $A = K_d$ is HPR proportionality constant, $B = K_t [2hH_m / RT_r]$, $C = K_d [2hH_m / RT_r]$, K_t is a constant, h is atomic diameter in the case of metal, H_m is the bulk melting enthalpy, R is ideal gas constant, T_r is the room temperature, $K_d > 100K_t$ and $\sigma_0 > 10K_t$.

The stochastic counterparts of equation (1) to (13) are considered to take care of their random fluctuations inherited from the random grain sizes in the nanomaterials during grain refinement. The resulting equations are solved simultaneously using Engineering Equation Solver software (F-Chart Software, Madison, W153744, USA). The data from (nanocrystalline) aluminium sample (some of which are found in other papers (Tengen, 2008:40) are used to validate models, which are

$M_0' = 0.01 \text{ nm}^2 \text{ s}^{-1}$, $m = 4$, $rc_1 = 1.95r$, $CC = 12$, $a = 0.90$, $D = 10^{-4}$, $h_0 = 0.25 \text{ nm}$, $T_m(\infty) = 933.47 \text{ K}$, $CV_0 = 0.3$, $H_m(\infty) = 10.71 \text{ kJ mol}^{-1}$, $\sigma_0' = 16.7 \text{ MPa}$, $K_t = 1.3$, $\sigma_0 = 15.40 \text{ MPa}$, $K_d = 1301.77 \text{ MPa nm}^{1/2}$, $R = 8.31 \text{ JK}^{-1} \text{ mol}^{-1}$ and $T_r = 300 \text{ K}$, $KB = 1.381023 \text{ J/K}$.

III. RESULTS AND DISCUSSION

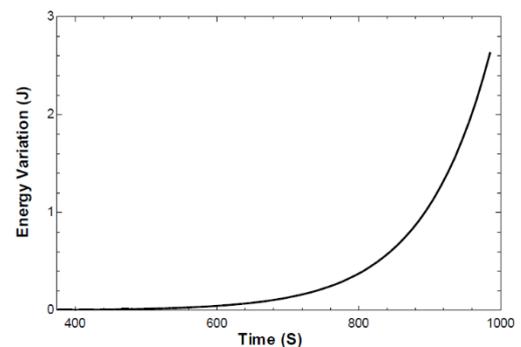
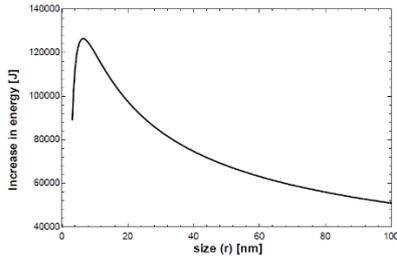


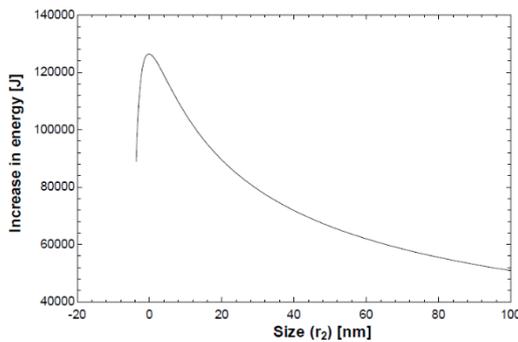
Figure 3: Energy variation and time

Previous theoretical studies of thermodynamics and mechanical properties focused on structure, shape, processing routes and defects in developing the relevant model of thermodynamic and mechanical property. The approach adopted in this current study is similar but more emphasis is focused on varying grain sizes, atomic radius r_0 , the density is ρ_0 , the particle radius, the average gyration radius, the average density, the overall number of atom in the particle N , atomic packing factor and the overall volume of atom in the cell and volume of atom in the cell. The results in Fig.3 revealed that as time increases during grain refinement the energy variation in the material increases. The increase in energy variation as time increases could be explain due to the following reason. During the process of grain refinement by ARB process more dislocation takes place in the grain boundaries of the materials after several ARB passes, and this happened after an increase in deformation time. This causes an increase in energy variation

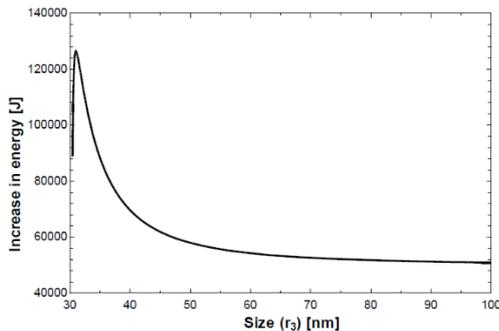
and an increase in time during ARB process as shown in Fig.3. Materials dislocation motions that are generated during ARB cycles vary in the different directions of measuring of the materials size and increase in energy during grain refinement by ARB as shown in Fig 4 (a-d).



(a)



(b)



(c)

Figure 4: Increase in energy and (a) size (r) (b) size r2 (c) size (r3).

It is observed as shown in Fig.4 (a-c) that all the evolution of size and increase in energy in the material during grain refinement evolved in a similar trend of Hall Petch to Reverse Hall Petch relationship during ARB. The results show that as sizes decreases the internal energy in the material increases to a very high internal energy which was immediately accompanied by drop in internal energy since the material could relax.

The increase in internal energy due to decrease in material size could be explained as follows; as the ARB cycles increases during grain refinement, more dislocation motion is generated

in the material which leads to an increase in energy of the materials. However, there are different rate of evolution of increase in energy and size during ARB process as observed in Fig.4 (a-c). The increase in energy evolved at a higher rate in r and r2 and at a very low rate in r3 as shown in Fig.4 (a-c) due to different dislocation motions as functions of the material size variants during ARB. The increase in energy with decrease in grain size can be explained since during grain refinement, the crystalline materials are being “squeezed” due to high compression subjected to the material. The “piezo” (push) effects on the material affect the grain dislocation, grain boundaries and grain mobility of atom. The grain boundaries become larger as the grain size decrease which impacts the increase in energy of the material. The mobility of free electrons and atoms also increases which impacts the increase in energy of the materials and this impacted the material property shown in Fig.5.

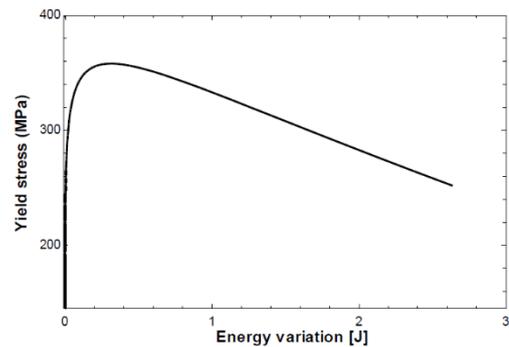


Figure 5: Energy variation and yield stress

The results in Fig.5 revealed that at very low energy variation the yield stress increases to an optimal yield stress and started decreasing at a steady rate due to increase in energy variation during ARB. This can be explained due to the following reason. Nanomaterials are very sensitive to temperature and energy since the mobility of atoms are very random at high energy and this also affect grain boundaries migration since grain growth begins to take place at elevated temperature due to adiabatic warming. Therefore, to achieve properties enhancement in nanomaterial produced by ARB, the effect of size, temperature and increase in energy must be well investigated and monitored.

IV. CONCLUSION

The current study was aimed at studying the effect of size on increase in energy and the impact in yield stress during ARB. To achieve this research objective the relevant theoretical models for increase in internal energy and change in sizes during ARB process was derived. The following facts were theoretically revealed by the model results. It was shown that as time increases during grain refinement the energy variation in the material increases. The increase in energy variation and time increases was due to dislocation that takes place in the grain boundaries during ARB passes. It was also shown that the evolution of size and increase in energy in the material during grain refinement is like the Hall Petch and Reverse Hall Petch

relationship during ARB. It was shown that as sizes decreases the internal energy in the material increases to a very high internal energy which was immediately accompanied by drop in internal energy since the material could relax. The increase in energy evolved at a higher rate in r and r_2 and at a very low rate in r_3 . The increase in energy with decrease in grain size was due to high compression subjected to the material.

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