Thermodynamics modeling of cohesive energy of metallic nano-structured materials

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HIGHLIGHTS
- A new modeling approach has been proposed to explain cohesive energy of metallic nano-structured materials (NSMs).
- The model outputs could justify the abnormal behaviors of NSMs.
- The model can be used for estimating any physicochemical properties of NSMs, related to cohesion energy.

GRAPHICAL ABSTRACT

ABSTRACT
A new modeling approach based on thermodynamics has been proposed to explain cohesive energy of metallic nano-structured materials. It was assumed that the nano-structured materials are nano-composites in which nano-crystals act as reinforcements embedded either in a disordered matrix, such as grain boundary area, or an ordered matrix, such as a crystalline metal. Then, cohesive energy of each part of the nano-composites including nano-crystallites, interfaces between these parts and grain boundaries in addition to inner structure of grain boundaries modeled individually considering the effect of size of nano-crystals as well as the effect of crystallinity of the matrix. The results of these calculations on the example of Au have been presented. On the basis of these calculations, the model outputs were in good agreement with predictions and reported abnormal behaviors of nano-structured materials in the literature such as superheating, in nano-composites, and decrease in melting point as a result of decrease in crystallite size, in metallic nano-structures.

1. Introduction
Nano-structured materials (NSMs) are assembled of nano-meter-sized building blocks, mostly crystallites. If the building blocks are crystallites, incoherent or coherent interfaces may be formed between them, depending on the atomic structure, the crystallographic orientation and/or the chemical composition of adjacent crystallites. In other words, materials assembled of nano-meter-sized building blocks are microstructurally heterogeneous consisting of the building blocks (e.g. crystallites) and the regions between adjacent building blocks (e.g. grain boundaries). It is this inherently heterogeneous structure on a nano-meter scale that is crucial for many of their properties and distinguishes them from glasses, gels, etc. that are microstructurally homogeneous [1–7].

One of the prominent effective characteristics of nano-materials is the size of their building blocks. Generally, in nano-materials, by reducing the size, the ratio of the surface to the volume of atoms/molecules increases which causes the interfacial energies to have a dominant effect on most of their unique chemical and physical behaviors, such as higher chemical activity and lower melting point. This has been established that these behaviors are related to the inner structural energy in materials and how strongly atoms/molecules stick together.

Please cite this article as: M.S. Yaghmaee, H. Ahmadian Baghbaderani, Thermodynamics modeling of cohesive energy of metallic nano-structured materials, Materials and Design (2016), http://dx.doi.org/10.1016/j.matdes.2016.10.067
dependent properties were just evaluated by experiments [11, 12] and collection of the particles [5]. But, as far as NSMs are concerned, the size-dependent properties of nano-particles (NPs) and NSMs are one of the most important fundamentals in nano-science and nanotechnology [4–7, 9].

In the case of NPs, most of the models deal with a free-standing single particle [6–8, 10, 11]. Also, in some cases the behavior generalized to the collection of the particles [5]. But, as far as NSMs are concerned, the size-dependent properties were just evaluated by experiments [11, 12] and theoretical facets of variation of their properties as a result of size reduction has been less studied which can justly attributed to the involved structure of grain boundaries and its both crucial and complicated effect on NSMs’ properties.

In this regard, a high density of grain boundaries is one reason why nano-crystalline materials have unconventional properties, so grain boundaries can have a great contribution to the size-dependent properties of NSMs. As a matter of fact, it has been well established that by decrease in the characteristic size of the nano-structures the fractional amount of grain boundary component increases drastically [13, 14], highlighting the importance of this microstructural component in NSMs’ properties.

Additionally, issues related to the structure of GBs have triggered many controversial discussions among scientists [8, 15]. Previous experiments on nano-crystalline materials have indicated that their grain boundaries (GBs) may differ from those of conventional polycrystalline materials, where just one or two layers of atoms form grain boundaries, due to the fact that NSMs contain many atoms at and near grain boundaries [13, 14, 16]. For example, a non-equilibrium low density structure has been proposed [17], but later experimental work is indicating that the grain boundaries are of high density, and not too different from those in coarse grained metals [18]. Then, Keblinski et al. [19] found that the grain boundary structure is amorphous without much structure. They obtained this result by analyzing the radial pair-distribution function of the atoms in the grain boundaries. They also showed the same phenomenon as far as silicon is concerned using molecular dynamics. Their results suggest that nano-crystalline silicon may be treated as a two-phase system, namely, an ordered crystalline phase in the grain interiors connected by an amorphous, intergranular glue-like phase [20]. In this study, the structure of grain boundaries is regarded as amorphous one although to fulfill different theories about the structure of GBs, the degree of amorphism of GBs is changeable.

Thus, based on such findings as well as inquiries in this field, this work represents a contribution along the estimation of cohesive energy of NSMs. It focuses, in particular, on size-dependent nature of this parameter. For this sake, a simple thermodynamic model for understanding the relationship between cohesive energy, microstructure and characteristic size inside NSMs is proposed.

2. Thermodynamic modeling

To elucidate the complicated structure of a NSM, it is considered as a nano-composite comprising nano-reinforcements which dispersed in a matrix (Fig. 1). The reinforcements of the nano-composite are nano-crystallites which have surface atoms with different amount of energy compared with inner ones (Fig. 1). The nano-crystallites are dispersed in a three-dimensional network, as the matrix of the nano-composite. The network can have either a disordered structure, e.g. grain boundary (GB) areas in metallic NSMs such as productions of mechanical alloying process [15, 21], or crystalline structure, e.g. in nano-composites including NPs embedded in a crystalline matrix [22, 23]. In the former, the structure of GB area can be considered as an amorphous structure.

2.1. Cohesion energy of nano-structured materials

For the purpose of modeling the cohesion energy of NSMs as nano-composites, it is needed to evaluate the cohesive energy of nano-crystallites, as nano-reinforcements, and the energy of grain boundaries as the matrix.

2.1.1. Cohesion energy of nano-crystallites

Nano-reinforcements representing nano-crystallines in NSMs can be considered as dispersed nano-particles. The size dependency of cohesion energy of the metallic nano-particles was calculated in the previously published paper of the first author [8], as:

\[ E_{\text{NP}}(D) = \left(1 - \frac{d_a}{D}\right) E_b(T) \]  \( \text{Eq. (1)} \)

where \( E_{\text{NP}} \) is the cohesion energy of a nano-particle (NP) in [kJ/mol] which is a function of \( D \) as the size (diameter) of the nano-particle in [m], \( d_a \) denotes atomic diameter of the nano-particle in [m], \( f_v \) is packing factor, and \( E_b \) represents bulk cohesion energy of the nano-particle’s material at macro-scale in [kJ/mol] which is dependent on \( T \) as temperature. Regarding Eq. (1), it should be noticed that, by decreasing the size of the nano-particle down to just very few atoms, the volume packing factor \( f_v \) will be meaningless, thus Eq. (1) should not be evaluated for the condition \( D = d_a \) [8].

2.1.2. Grain boundary energy at nano-scale

GB areas play a multifaceted role as far as cohesive energy of NSMs is concerned. For instance, GBs have a prominent influence on the surface energy of nano-crystallites as it is in direct contact with the surface of nano-crystallites. Furthermore, inner structure of GBs has its own energy level. In the current model all of these factors are summarized as GBs’

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Fig. 1. Schematic of NSMs’ microstructure.
energy. However, as a result of the fact that total energy of the NSMs is the summation of crystallites’ energies in addition to all as-mentioned energies, this categorization makes no difference in final amount of NSMs’ energy.

Based on this arrangement, this section is divided into three parts, in the first part the interfacial energies of nano-crystallites and its possible size dependency at nano-scale are investigated, whereas at the second part the energetic interaction between nano-crystallites and grain boundaries is discussed and at the third part cohesion energy of inner structure of grain boundaries, as matrix of the composite, is calculated which all lead to proposing a simple model for evaluation of grain boundary energy at nano-scale.

2.1.2.1. Surface energy of nano-crystallites. Surface energy, \( \sigma_s \) (between solid and gas phase), as one of the most important properties of condensed materials is mostly believed to be varied by size at nano-scale [24–29]. Reports showed either an enhancement in \( \sigma_s \) or a decline in \( \sigma_s \), e.g. in Zn, Pd and even Si in their tube shape [28,29], as a direct reason for decrease in their melting points. In contrast, there are some studies which disagree with any effect of size on the value of \( \sigma_s \) [30].

In the case of augment of surface energy as a result of decline in nanoparticles size, a model was developed for the surface energy of fcc metallic nanoparticles [31]. Based on this model, it was found that the surface energy has a slight reduction firstly and turn back to increase when the size approaches to critical size of particles. The reduction of surface energy was mainly attributed to the decrease of cohesive energy and the following increase was owing to the decrease in surface coordination number. Moreover, in another study [32], a theoretical analysis was carried out for various fcc metallic nanoparticles. As a result, it has been proven that the surface energy density decreases with the increase of nanoparticle diameter. Motivated by often contradictory literature reports on size dependence of surface energy of gold nanoparticles, Holec et al. [33] performed an atomistic study combining molecular dynamics and ab initio calculations. This study has found an increase of the surface energy with decreasing particle size.

As other theoretical studies [31–33], an increase was observed in \( \sigma_s \) of Ag and Au from 1.25 to 1.5 and 9–9.3 J/m² respectively [24–26]. Thus, regarding as-mentioned reports the enhancement of the quantity is more likely to happen and seems to be explainable by other properties of nano-materials as well. Thus, considering the rise in \( \sigma_s \) of Au, from 1.5 to 9.3 J/m² [24], a coefficient in the range of 6–6.2 can be predicted. Using this coefficient, the \( \sigma_s \) for Au would reach to 7.2 J/m² from its bulk quantity of 1.25 J/m² which is in good agreement with experimental and theoretical proof in [25,26].

2.1.2.2. Interaction between nano-crystallites and grain boundaries. Energy of such interaction is evaluated from a basic point of view. In this regard, after separating a solid phase from a liquid one inside a gas phase, the theory of Young-Dupre defines the value of adhesion energy between solid and liquid (\( W_{s-l}/[m^2] \)) by \( \sigma_{slg} = \sigma_{sg} - \sigma_{lg} \), where \( \sigma \) is the surface energy in [J/m²] and \( s.l.g \) symbolize the state of materials being solid, liquid and gas respectively.

Regarding this theory, to calculate the required energy for dividing a solid material into two parts, the terms related to the liquid phase in Young-Dupre theory must be substituted with the ones belonged to solid phase. Thus, \( W_{s-l} \) in surface energy scale can be written as \( \sigma_{slg} \), and since there is no energy difference between two surfaces of a material, thus, we can write:

\[
\sigma_{slg} = 0 \quad \Rightarrow \quad W_{s-l} = 2\sigma_{sg} \quad (2)
\]

Considering the definition of surface energy in [34] and illustration of Fig. 2, the adhesion originated from two parts of a material is nothing than the cohesive energy inside the materials. In addition, to make the theory more applicable, a given area of material can be introduced into the formulas as follow,

\[
wW_{s-l} = \frac{E}{C_1} \quad \Rightarrow \quad E = \frac{2w\sigma_{sg} [kJ/mol]}{C_1} \Rightarrow \quad E = 2\sigma_{sg} [kJ/mol] \quad (3)
\]

where \( w \) is the surface molar area in [m²/mol], \( A \) is the actual area in [m²], \( E_m \) denotes as surface molar energy of material in [kJ/mol] and \( E \) is total surface energy for the specific area \( (A) \) of material.

In Eq. (3), \( 2\sigma_{sg} \) symbolizes the summation of two \( \sigma_{sg} \) of two separated surfaces which are the surface of crystallites and GBs in the case of NSMs (Fig. 2), so

\[
E = A\left(\sigma_{slg} + \sigma_{slg}^{np} \right) [kJ] \quad (4)
\]

Grain boundary in a solid crystalline material is a region joining two crystals of the same phase which differ in mutual orientations and the grain boundary thus represents a transition region which its first layer has a similar atomic structure with surface of crystal. Otherwise, to attain a suitable contact with the crystals and to accommodate the misorientation between two adjoining crystals, an array of dislocations can be formed on the surface of crystals [35]. Because of the mutual effect of strain field of dislocations on the surface of crystals as well as grain boundaries, and as-mentioned similarities on their surface atomic structure, the surface energy of these two components can be estimated as equal to each other and Eq. (4), which represents the total amount of energy as a result of interaction between crystallites and grain boundaries, can be written as,

\[
E = 2\sigma_{sg}^{np} [kJ/mol] \quad (5)
\]

2.1.2.3. Cohesion energy of inner structure of grain boundaries. As it is mentioned in introduction section, the structure of grain boundaries is considered as amorphous one, while the degree of amorphousness of GBs is changeable. To begin with, the influence of the amorphous structure on the physicochemical properties of bulk metals in particular about cohesion energy of polycrystalline metals must be evaluated, but there are a few published articles, such as [36,37]. In this case, therefore, regarding the results reported in [37], which deals with the effect of cohesion of amorphous state on physical properties of metals, and

![Fig. 2. Schematic presentation of the energy model for surface interaction of a crystallite and GB.](image)
the previously published paper of the first author on polycrystalline metals [36], a simple ratio factor for evaluation of the role of inner cohesive energy of grain boundaries, as an amorphous structure, on the total cohesion energy of NSMs in the following manner is considered.

For this purpose, Jeffries' theories in [37] are regarded as a basis of the current model. Briefly these theories are;

a. cohesion energy \( E \) of amorphous state at melting point tends to zero. It is worth mentioning that here zero is a relative quantity which is a sign of solid-liquid transformation as a result of demolition of some of integral bonds.

b. by decrease in temperature, the cohesion energy of the amorphous state of metallic elements increases even with the faster rate than the crystalline state; To elucidate this claim more, it should be mentioned that based on the hypothesis which mentioned above the structure of Bulk Metallic Glasses (BMGs) are the most similar structures to the GBs’ ones and it has been established that BMGs exhibit higher strength and hardness compared to their crystalline counterparts [38–40], which is believed to be associated with the cohesive strength between atoms and/or atomic clusters [39,41–43].

c. there is a temperature where the cohesion of these two states: crystalline and amorphous, have cross-section which this point is called Equi-Cohesive point (EC),

d. in most metals this temperature is within the range of 0.35 \( T_m \) and 0.45 \( T_m \),

e. at temperatures lower than EC the amorphous state not only has stronger cohesion energy, but also the cohesion energy experiences higher increasing rate as temperature decreases further,

f. EC is related to the temperature of re-crystallization and cold working. Therefore, under 0.35 \( T_m \) as temperature decreases amorphous state of metals, due to some kind of disordering mechanism and decrease in atomic motion, could be considered as relatively more stable structure in comparison with crystalline ones [44,45]. To clarify the discussion more, schematic illustration in Fig. 3 presents the aforementioned conclusions in [37], the inter relation between the cohesion and strength, and the relation between EC and mechanical properties of amorphous metals reported by [46]. It should be mentioned that due to the fact that metallic elements behave regarding their bonding in a similar manner, this kind of conclusion regardless on numbers (without any quantities) are used to be applied in extrapolating the behavior of other metals, as long as there is no contradiction [8,47,48]. Therefore, as a conclusion of the as-mentioned theory it can be written,

\[
E_{\text{matrix}} = yE_b \quad \text{when} \quad \begin{cases} y < 1 & \Rightarrow E_{\text{amorphous}} < E_b \\
y = 1 & \Rightarrow E_{\text{amorphous}} = E_b \quad \text{at a point } 0.35T_m < T < 0.45T_m \\
y > 1 & \Rightarrow E_{\text{amorphous}} > E_b \quad \text{when } 0 < T < 0.35T_m 
\end{cases}
\]  

where \( y \) is the ratio representing the amorphousness of the matrix, which in NSMs is grain boundaries area. In other words, this ratio is equal to amount of matrix’s cohesive energy with respect to total crystalline state’s energy as evaluated in [36] by \( E_b \).

Regarding the linear relation between cohesion energy and melting temperature [36] and to define cohesion energy using some tangible variables, for cohesion at 0 K and \( T_m \) it can be written,

\[
E_{b,T_m} = \alpha T_m \quad \text{and} \quad E_{b,0} = \beta T_m \quad \text{where} \quad \beta > \alpha \quad (7)
\]

where \( \alpha, \beta \) are the equality constants in [kJ/mol K]. Fig. 4 shows the calculation of Eq. (7) for different metals [36]. For more and detailed information, it is suggested to check the published theory of the same author in [47].

Evaluated values of \( \alpha, \beta \) in Fig. 4, as Eq. (7) represented, leads to: at \( T = 0 \) K, \( E_{b,0} = 0.287T_m \) and at \( T = T_m \) K, \( E_{b,T_m} = 0.256T_m \). Furthermore, if two rectangular triangles with vertices of \( T_m, T = 0 \), \( E_{\text{amorphous},0} \) and \( T_m, T = 0, E_{\text{amorphous},0} \) in Fig. 3 are considered, based on similar triangles law, Eqs. (8) and (9) can be extracted, respectively;

\[
\begin{align*}
\frac{T_m}{T_m - 0.35T_m} &= \frac{E_{\text{amorphous},0}}{E_b} \Rightarrow E_{\text{amorphous},0} = 1.538E_b0.35T_m \quad (8) \\
\ldots \Rightarrow E_{\text{amorphous},0} &= 1.818E_b0.45T_m \quad (9)
\end{align*}
\]

The maximum difference between two state of amorphousness in Eqs. (8) and (9) at 0 K can be written as,

\[
E_{\text{amorphous},0} - E_{\text{amorphous},0} = 1.818E_b0.45T_m - 1.538E_b0.35T_m \quad (10)
\]

Regarding numerical calculation of the proposed hypothesis in [37] and estimated data in [36], dealing with cohesive energy of metallic structures in ideal state, and as far as Fig. 3 and the algorithm behind it, is concerned, it seems to be likely to calculate the range of cohesive energy of amorphous state for every metals. Fig. 5 gives information about how this data can be calculated for three different metals comprising Na, Mg and Fe with absolutely different melting temperatures: low, moderate and high respectively.

Moreover, considering the rectangle with vertices of \( E_{b,T_m}, E_{b,0}, T = 0 \) and \( T_m \) in Fig. 5 and regarding Eq. (7), it can be written,

\[
\frac{E_{b,T_m} - \alpha T_m}{\beta T_m - \alpha T_m} = \frac{T - T_m}{T_m - 0} \Rightarrow E_{b} - \alpha T_m = \left(T - T_m\right)\left(\alpha - \beta\right) \quad (11)
\]
where

\[
E_b(T) \approx (\alpha - \beta)T + \beta T_m = \beta (T_m - T) + \alpha T \tag{12}
\]

and considering values of \(\alpha, \beta\) in Fig. 4,

\[
E_b(T) \approx 0.287(T_m - T) + 0.256T_m \tag{13}
\]

where considering Eq. (10) and regarding the linear temperature dependency of \(E_b(T)\) from Eq. (13) it can be written,

\[
E_{0.45T_m}^{\text{amorphous,0}} - E_{0.35T_m}^{\text{amorphous,0}} = 1.818 \left[ E_b(0.45T_m) - 1.538 \left[ E_b(0.35T_m) \right] \right] \tag{14}
\]

and

\[
E_{0.35T_m}^{\text{amorphous,0}} - E_{0.45T_m}^{\text{amorphous,0}} = 0.071T_m \tag{15}
\]

This difference, 0.071 \(T_m\), attributes to 0 K, so easily from Figs. 3 and 4, the temperature dependency curve for two amorphous state of 0.45 \(T_m\) and 0.35 \(T_m\) can be written as follows, respectively,

\[
E_{0.45T_m}^{\text{amorphous}}(T) = \left(1 - \frac{T}{T_m}\right)1.818E_b(0.45T_m) = \left(1 - \frac{T}{T_m}\right)E_{0.45T_m}^{\text{amorphous,0}} \tag{16}
\]

and

\[
E_{0.35T_m}^{\text{amorphous}}(T) = \left(1 - \frac{T}{T_m}\right)1.538E_b(0.35T_m) = \left(1 - \frac{T}{T_m}\right)E_{0.35T_m}^{\text{amorphous,0}} \tag{17}
\]

Therefore, the maximum value of cohesion energy when \(T < 0.35T_m\) can be 1.818 \(E_{0.45T_m}\) or 1.538 \(E_{0.35T_m}\), while at high temperature 0.45 \(T_m < T\) the amount of amorphous cohesion energy can be as low as \(E_{0.45T_m}\). Moreover, if the limiting value of 1.538 \(E_{0.35T_m}\) from Eqs. (8) and (13) is evaluated, it can be concluded,

\[
E_{0.35T_m}^{\text{amorphous,0}} = 1.538E_b(0.35T_m) = 1.538 \left[ 0.287(T_m - 0.35T_m) + 0.256 \times 0.35T_m \right] = T_m \left[ 0.287 + 1.538 - 0.287 \times 0.35 + 1.538 \times 0.256 - 0.35 \times 1.538 \right] = 0.424T_m \tag{18}
\]

and regarding the relation between melting point and cohesion energy in [36],

\[
E_{0.35T_m}^{\text{amorphous,0}} = 0.424T_m \approx 0.424 \times 4.04 \times E_{0.0K} \approx 2E_{0.0K} \tag{19}
\]

As it can be seen in Eq. (19), the maximum value of cohesion energy of amorphous state is twice as high as cohesive energy of crystalline one. This estimation using the 0.45 \(T_m\) curve from Eq. (9) instead of Eq. (8) leads to a number which is only 0.030\(E_b\) more than calculated amount in Eq. (8). To sum up, even if the whole matrix reaches the amorphous state the cohesion energy reaches to 2\(E_b\) with respect to total crystalline state energy, \(E_{0.0K}\). Thus, in this paper at 0 K the range of (1.5 - 2)\(E_b\) is attributed to the maximum value of amorphous cohesion and at melting point, the range of (0 - 0.5)\(E_b\) is considered as the lowest value of amorphous cohesion energy. Therefore, \(y\) as a ratio in Eq. (6), represents the proportion of amorphous state energy to crystalline ones which is in 0 \(\leq y \leq 0.5\) and 1.5 \(\leq y \leq 2\) intervals.

### 2.1.3. Modeling the whole nano-structured material

The cohesion energy of NSMs consists of three terms of; i. summation of inner cohesion energies of all NPs, as nano-crystals, to be evaluated using Eq. (1), ii. excess energy due to interfacial boundary between NPs and matrix, as grain boundaries, as modeled by Eq. (5). iii. cohesion energy of matrix as a macro-scale phenomenon which can be calculated regarding its amorphous to crystalline amount by Eq. (6), the summation of terms ii and iii is regarded as grain boundary energy. As far as the mass conservation law \((n_{\text{matrix}} + Xn_{\text{NP}} = n_{\text{total}})\) is concerned, these energy terms can be hypothesised in the following mathematical expression for particular NSM in [kJ], as,

\[
E_{\text{material}} = Xn_{\text{NP}}E_{\text{NP}} + \left(2X \frac{A_{\text{NP}}}{n_{\text{total}}} \right)E_{\text{NP}} + \left(\frac{n_{\text{matrix}}}{n_{\text{total}}}\right)E_{\text{matrix}} \tag{20}
\]

where \(n\) denotes the number of moles and \(X\) is the mole-fraction. Although in a particular example; the area of nano-particles \((A_{\text{NP}})\), the number of moles of these components \((n_{\text{NP}})\) and even number of mole of matrix \((n_{\text{matrix}})\) are each indirectly size dependent quantities, \(f(D)\):

\[
\begin{align*}
\left( \begin{array}{c}
A_{\text{NP}} \\
X_{\text{NP}} \\
n_{\text{matrix}}
\end{array} \right) &= f(D) \\
\frac{A_{\text{NP}}}{n_{\text{total}}} &= f(D) \\
\frac{n_{\text{matrix}}}{n_{\text{total}}} &= f(D)
\end{align*}
\tag{21}
\]
where \( m \) is the mass of NPs in [g]; \( M \) is molar mass of NPs in [g/mol]; \( V \) is volume of NPs in [cm\(^3\)]; and \( \rho \) is the density of NPs in [g/cm\(^3\)]. Moreover, in Eq. (20) we can principally check the boundary conditions of this hypothesis, as:

i- by decreasing the number of NPs we have to reach the bulk cohesion energy,

\[
\text{if } X = 0 \Rightarrow E_{\text{material}} \rightarrow E_{\text{matrix}} + 0 + 0 = E_{\text{material}} \rightarrow E_{\text{matrix}}
\] (22)

ii- by decreasing the amount of matrix, when we have one NP, we have to reach the cohesion energy of free standing NP:

\[
\text{if no matrix } \& \ X = 1 \Rightarrow E_{\text{material}} \rightarrow 0 + E_{\text{NP}} + 0 = E_{\text{material}} \rightarrow E_{\text{NP}}
\] (23)

As mentioned above the matrix of this composite (as NSM) can have either amorphous or crystalline structure. Owing to dependence of the cohesive energy to the structure of materials as described in Eq. (6), by defining the correction coefficient, the model can predict the effect of crystallinity of the matrix on total cohesive energy of composite, as,

\[
\Rightarrow \text{Eq. (20) } \text{3rd term} = \frac{n_{\text{matrix}}}{n_{\text{total}}} y E_b
\] (24)

Considering the effect of size on the energy of NPs, Eq. (1), it can be written:

\[
\text{Eq. (20) } \text{1st + 3rd terms} = \frac{n_{\text{NP}}}{n_{\text{total}}} E_b \left(1 - \frac{d_a}{\gamma D} \right) + y \frac{n_{\text{matrix}}}{n_{\text{total}}} E_b
\] (25)

If \( y \rightarrow 1 - (1 - y) \Rightarrow \)

\[
\text{Eq. (20) } \text{1st + 2nd terms} = \frac{n_{\text{NP}}}{n_{\text{total}}} E_b \left(1 - \frac{d_a}{\gamma D} \right) + \left(\frac{n_{\text{matrix}} + n_{\text{NP}}}{n_{\text{total}}} E_b \right) + (1-y) \frac{n_{\text{matrix}}}{n_{\text{total}}} E_b
\] (26)

and by rearranging the terms,

\[
\text{Eq. (20) } \text{1st + 3rd terms} \rightarrow \frac{n_{\text{NP}}}{n_{\text{total}}} E_b \left(1 - \frac{d_a}{\gamma D} \right) + \left(2 \times \frac{A}{n_{\text{total}}} \right) \sigma_{\text{NP}} + E_b
\]

\[
+ (1-y) \frac{n_{\text{matrix}}}{n_{\text{total}}} E_b
\] (27)

Therefore, by substituting the Eq. (5) instead of 2nd term in Eq. (20), and considering Eq. (27) we can rewrite Eq. (20), as:

\[
E_{\text{material}} = \frac{n_{\text{NP}}}{n_{\text{total}}} E_b \left(1 - \frac{d_a}{\gamma D} \right) + \left(2 \times \frac{A}{n_{\text{total}}} \right) \sigma_{\text{NP}} + E_b
\]

\[
+ (1-y) \frac{n_{\text{matrix}}}{n_{\text{total}}} E_b
\] (28)

Using Eq. (28) and substituting the basic thermodynamic data of NSMs, the effect of crystallinity of matrix, amount of NPs, size of NPs of a particular material with given \( d_a, \gamma, \sigma_{NP} \) and \( E_b \) values on the total cohesion energy of composites (NSMs) can be estimated.

### 3. Computational analysis

Spherical and decahedron nano-crystallites of Au with two variant surface energies embedded in two different matrix structures were considered for evaluation of the proposed model, Eq. 28. Some of the structural, physical and thermodynamic data of Au used in the model are listed in Table 1. Moreover, NSMs’ properties such as amorphousness/crystallinity ratio, number of mole and size of NPs, or nano-crystallites, and total mole of NSMs are listed in the figure of each section.

#### 3.1. Spherical Au NPs with bulk surface energy in crystalline matrix at 0 K

In this section, the cohesion energy of a nano-composite comprising Au nano-crystals at different sizes: 100, 50 and 10 nm, embedded in a crystalline Au matrix was evaluated. These sizes were chosen to have a general picture of the trend of cohesion energy in the range of 0–100 nm. As a matter of fact, it is supposed that abnormal behavior of

### Table 1

Primary structural, physical and thermodynamic data of Au in fcc structure.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume packing factor</td>
<td>0.74</td>
</tr>
<tr>
<td>Atomic radius ( d_a ) [pm]</td>
<td>144</td>
</tr>
<tr>
<td>Molar mass ( M ) [g/mol]</td>
<td>196.966</td>
</tr>
<tr>
<td>Density ( \rho ) [g/cm(^3)]</td>
<td>19.32</td>
</tr>
<tr>
<td>Molar volume ( V_m ) [m(^3)/mol]</td>
<td>10.2 × 10(^{-6})</td>
</tr>
<tr>
<td>Molar surface area ( w ) [m(^2)/mol]</td>
<td>72,904, (110); 103,095, (111); 64,439</td>
</tr>
<tr>
<td>Cohesion energy at 0 K [kJ/mol]</td>
<td>379.05</td>
</tr>
<tr>
<td>Cohesion energy at 500 K [kJ/mol]</td>
<td>353.852</td>
</tr>
</tbody>
</table>

Fig. 6. Calculated results of two size-dependent terms in Eq. (28) and total cohesion energy for 1 mol of nano-structured Au as a function of number of spherical NPs at different sizes: 100, 50 and 10 nm, when the nano-structure comprised of particles with bulk surface free energy (1.5 J/m\(^2\)) embedded in a crystalline matrix (\( y = 1 \)).

Please cite this article as: M.S. Yaghmaee, H. Ahmadian Baghbaderani, Thermodynamics modeling of cohesive energy of metallic nano-structured materials, Materials and Design (2016), http://dx.doi.org/10.1016/j.matdes.2016.10.067
nanomaterials can be noticed when the size of their building blocks is below 100 nm, critical size, and consequently to follow the changes in as-mentioned range two other sizes, 50 nm and 10 nm, were taken into account. In these calculations, the impact of number of Au NPs was also considered (Fig. 6), which is related to the thickness of interfacial area of the matrix. Fig. 7 shows the total cohesion of Au at fixed $10^{18}$, $10^{20}$ and $10^{21}$ NPs for 1 mol of material as a function of particle size between 100 and 1 nm. As it can be seen by increasing the amount of NPs and decreasing their size the total cohesion energy of NSM decreases and reaches the low of 367.6 kJ/mol which is about 11.5 kJ/mol or 3.02% lower than bulk crystalline Au. Moreover, in contrast to the majority of the results recorded in the literature predicting higher surface energy for NSM, in [49] lower Debye temperature has been estimated and it was attributed to lower $C_v$ (in contradiction to [50]) which is a consequence of lower cohesion energy, as shown by this model, Figs. 6 and 7.

3.2. Spherical Au NPs with enhanced surface energy in crystalline matrix at 0 K

These sets of calculations show the effect of higher surface energy of Au NPs, compared to their bulk counterparts, on the total cohesion energy of Au NSMs (Fig. 8). By increasing the amount of NPs and decreasing their size the total cohesion energy increases and for 2 nm nanoparticles there is a maximum difference of 86.56 kJ/mol between the energy level of nano-particles and bulk (Fig. 8). This phenomenon was verified in the literature and it is called super-heating [51,52]. Therefore, the behaviors of the different nano-composites depend on variety of parameters. Based on observed differences in Figs. 7–8, one of the prominent parameters is the surface energy of nano-crystallites. Due to the fact that higher surface energy of nano-crystallites is closer to the real situation, so the results of the model in this section are consistent with experimental results and the model can justify superheating as a
phenomenal effect as far as nano-structures is concerned. Additionally, super-heating was mainly attributed to the nature of interface between the nano-crystallites and the matrix [51, 52]. Also, based on this model, surface energy which is a noticeable parameter in the quality of the formed interfaces has been shown as a key-factor.

3.3. Spherical Au NPs with enhanced surface energy in amorphous matrix (lower cohesion energy) at 0 K

As it was modeled in the 2.1.2.3 sub-section, cohesive energy of inner structure of the disordered matrix can be higher or lower than crystalline ones in the aforementioned intervals. Here the matrix is assumed to have a lower cohesion energy compared to crystalline Au. The effect of different amounts of Au NPs with different sizes: 100, 50 and 10 nm, on total cohesion of Au NSM has been evaluated in Fig. 9. Report of [53] regarding the effect of Sn particle size on its heat capacity shows that even decreasing the size from 50 to 7 nm does not shows any $C_v$ change which could be an indirect evidence for not changing the cohesion energy with size. Similar observation regarding the Fe$_2$O$_3$NSM in [54] shows that even at 13 nm there was not huge shift in $C_p$ of hematite. Also, results of our calculations in Figs. 9–10 verify these facts as well which means even in matrix with lower binding energy due to its disordered structure, by increasing the amount of NPs while decreasing their size the cohesion energy level of the bulk polycrystalline material is reachable.

3.4. Spherical Au NPs with enhanced surface energy in amorphous matrix (higher cohesion energy) at 0 K

The effect of size and amount of Au nano-crystallites on the total cohesion energy of Au NSM are studied. As it can be seen in Fig. 11, by...
increasing the amount of NPs and decreasing their size the total cohesion energy of NSM has been decreased. One of the main results of decrease in cohesion energy is reduction in the melting point. This achievement is in good agreement with melting temperature reduction in similar-structure NSMs in [9,12,55,56].

3.5. Decahedron Au NPs with enhanced surface energy in crystalline matrix at 500 K

The effect of temperature rise, up to 500 K, as well as shape of crystallites on the cohesion energy of Au NSM, as shown in Fig. 12, is studied. Au NPs shape was considered as decahedron with shape factor of 0.449 [57]. Moreover, enhanced surface free energy was considered while the matrix has been regarded as a crystalline matrix. Fig. 12 shows that although there is not any increase in the cohesion energy of the matrix material because it was considered as a crystalline matrix, there is a 41% (145 kJ/mol) increase in total cohesion energy for Au NSM at very small scale, 1–2 nm.

4. Conclusions

Metallic nano-structured materials (NSMs) were considered as nano-composites comprising nano-crystals (as their reinforcement) which dispersed in three-dimensional network (as their matrix). Based on this assumption, a simple thermodynamic model for prediction of cohesive energy of NSMs and studying the size-dependent nature of this parameter as a prominent property of materials was proposed. The influence of crystallinity of the matrix on the cohesive energy was studied, as well. It was shown that size contraction leads to decrease in cohesive energy of metallic NSMs with disordered matrix, which is justifiable based on a decrease in melting point of such materials due to crystallite size refinement. On the other hand, this trend was reverse for crystalline-matrix NSMs, which is consistent with

![Fig. 11. Calculated results of two size-dependent terms in Eq. (28) and total cohesion energy for 1 mol of nano-structured Au as a function of number of NPs at different sizes: 100, 50 and 10 nm, when the nano-structure comprised of nano-crystallites with higher surface free energy (9.3 J/m²) embedded in a matrix with higher binding energy (y = 1.5).](image_url)

![Fig. 12. Calculated results of total cohesion energy for 10^{18}, 10^{19} and 10^{20} decahedron Au NPs with higher surface energy (9.3 J/m²) at different particle size embedded in a crystalline matrix (y = 1) at 500 K.](image_url)
superheating phenomenon, so some of the abnormal behaviors of NSMs at nano-scale is explicable via the present model, while care must be taken in applying the model for different kinds of materials because of the assumptions which were considered during preparing the model. In this case, depending on the state of matrix (being crystalline or amorphous), size, shape and amount of nano-crystallites and the effect of interfaces between nano-crystallites and matrix, the cohesion energy of NSMs could be higher or lower than their bulk crystalline counterparts. The developed model in this study is suggested to be used for estimating any physicochemical properties of metallic NSMs which is related to cohes-

### Acknowledgement

This work has been supported in part by a research grant (No: 321390030) from Materials and Energy Research Center (MERC), Karaj, Iran.

### References

[8] M.S. Yaghmaee, B. Shokri, Effect of size on bulk and surface cohesion energy of metal-

Please cite this article as: M.S. Yaghmaee, H. Ahmadian Baghbaderani, Thermodynamics modeling of cohesive energy of metallic nano-structured materials, Materials and Design xxx (2016) xxx–xxx.