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Surface energy of metal alloy nanoparticles

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ABSTRACT

The measurement of surface energy of alloy nanoparticles experimentally is still a challenge therefore theoretical work is necessary to estimate its value. In continuation of our previous work on the calculation of the surface energy of pure metallic nanoparticles we have extended our work to calculate the surface energy of different alloy systems, namely, Co–Ni, Au–Cu, Cu–Al, Cu–Mg and Mo–Cs binary alloys. It is shown that the surface energy of metallic binary alloy decreases with decreasing particle size approaching relatively small values at small sizes. When both metals in the alloy obey the Hume–Rothery rules, the difference in the surface energy is small at the macroscopic as well as in the nano-scale. However when the alloy deviated from these rules the difference in surface energy is large in the macroscopic and in the nano scales. Interestingly when solid solution formation is not possible at the macroscopic scale according to the Hume–Rothery rules, it is shown it may form at the nano-scale. To our knowledge these findings here are presented for the first time and is challenging from fundamental as well as technological point of views.

1. Introduction

Nanotechnology is the art and engineering of manipulating matter at the nanoscale. Properties of materials of nanometric dimensions are significantly different from those of atoms as well as those of bulk materials. Decreasing material size into the nanoscale is accompanied by a drastic increase in surface area to volume ratio which leads to superior physical and chemical properties including mechanical, optical, electrical, catalytic and magnetic properties of the nanomaterial [1,2].

Metal alloys play a crucial role in modern society and a great deal of effort is expended to learn about their synthesis, properties, and processing to optimize their use in a wide range of applications. Part of these applications is related to surface properties of metal alloys which usually differ from that of the bulk and result from a vast number of configurations and type of surface sites that multi-component materials can afford. This phenomenon is referred to as surface segregation and it is largely controlled by the surface energy which is one of the key properties of metallic surfaces [3]. Determination of surface energy which can be interpreted as a reversible work per unit area involved in creating a new surface is important in understanding a wide range of surface phenomena including growth rate, formation of crystallites, sintering, catalytic behavior, adsorption, surface segregation, and the formation of grain boundaries [4].

The interest in studying alloy nanoparticles is due to their myriad chemical and physical properties that may be tuned by varying the composition and atomic ordering as well as the size of the nanoparticle clusters. Surface structures, compositions, and segregation properties of nanoalloys are of interest as they are important in determining chemical reactivity and especially catalytic activity [5]. Structures of binary metal alloys may be quite different from the structures of the corresponding pure elements of the same size and synergism is sometimes observed in catalysis by bimetallic nanoalloys [6]. For nanoparticles, a strong size effect of surface energy emerges when the particle diameter is less than a few nanometers but due to the small size of nanoparticles, it is very difficult to measure the surface energy experimentally [7]. Therefore, theoretical models and computer simulations are needed to study the surface energy at nanoscale.

In a previous work by Aqra and Ayyad [8] the surface energy of metallic nanoparticles was calculated based on a simple model assuming different shapes of particles. They found that surface energy reduces as the number of atoms decreases and the best fit with the reported values was observed when nanoparticles were assumed to have spherical shape. In this work an extension of the model is made to satisfy the requirements to theoretically calculate the surface energy of alloy nanoparticles at different sizes. The model output will be validated by comparing the obtained values with the available theoretical and experimental data.

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2. Theory background

A simple equation to calculate the surface energy of bulk solid metals was reported [8] and the derivation was based on the calculated surface tension of liquid metals and the predicted values were in good agreement with theoretical and experimental data [8,9]. The equation is:

$$\gamma_{SV} = \frac{1}{\vartheta}\left[0.195\frac{E_s}{N}\right] \quad (1)$$

whereγ_{SV} is the surface energy of a solid metal $\left(mJm^{-2}\right)$, E_s is the heat of sublimation $\left(Jmol^{-1}\right)$, N is Avogadro's number and ϑ is the area occupied by each metal atom $\left(m^2atom^{-1}\right)$ and 0.195 is a semi-empirical fitting parameter. To calculate the surface energy of a binary metal alloy Eq. (1) will be modified to the following form:

$$\gamma_{SV}^{alloy} = \frac{1}{\vartheta^{alloy}}\left[0.195\frac{E_s^{alloy}}{N}\right] \quad (2)$$

where $\vartheta^{alloy}$and $E_s^{alloy}$are the atomic area and sublimation energy of the alloy calculated by using the following equations:

$$\vartheta^{alloy} = \frac{\sqrt{3}}{2}\left(\frac{\sqrt{2}V_s^{alloy}}{N}\right) \quad (3)$$

where V_s^{alloy} is the molar volume of the alloy calculated from the molar volumes of the two pure metals at their melting points according to this equation [10]:

$$V_s^{alloy} = x_A V_s^A + x_B V_s^B \quad (4)$$

where x_A and x_B are the mole fractions of the two metals while V_s^A and $V_s^B$are the molar volumes of the two metals in their pure forms. The dissociation energy of the alloy at each mole fraction is calculated by the relation [11]:

$$E_s^{alloy} = x_A^2 E_s^A + x_B^2 E_s^B + 2x_A x_B\sqrt{E_s^A E_s^B} \quad (5)$$

The derived equation used to calculate the surface energy of nanoparticles was based on a couple of assumptions, among them that the metallic nanoparticles are spherical in shape and the atoms are closed packed within these nanoparticles with no space between them [8]. The working equation that was utilized to calculate the surface energy is:

$$\gamma_{particle} = \gamma_{SV}\left[1 - \frac{3}{4}\frac{\eta}{\rho^{2/3}}n_t^{-1/3}\right] \quad (6)$$

where $\gamma_{particle}$ is the surface energy of a metallic nanoparticle, η and ρ are two packing fraction parameters with the values of 0.74 and 0.9 respectively and n_t is the total number of atoms of the metallic nanoparticles.

3. Results and discussion

Since many properties of nanoparticles are not easily measured experimentally, theoretical models and computational methods are necessary to get insight into properties of these interesting systems including surface energy. The existing literature often contains conflicting and contradictory data pertaining to the surface energy of metal nanoparticles and the effect of particle size on the measured values [12]. The *binary metal* systems studied here were selected in a way that can give insight to the effect of their relative sizes of the atomic constituents of these alloys and their sublimation energies on the values of surface energy.

Table 1
Atomic radii and Pauling electronegativity for selected metals [15].

Element	Symbol	Radius (A°)	Pauling electronegativity
Magnesium	Mg	1.601	1.31
Aluminum	Al	1.432	1.61
Cobalt	Co	1.251	1.88
Nickel	Ni	1.246	1.91
Copper	Cu	1.278	1.90
Molybdenum	Mo	1.363	2.16
Cesium	Cs	2.650	0.79
Gold	Au	1.442	2.54

The first binary metal alloy that has been investigated consists of the two metals cobalt and nickel. This system is expected to fulfill the Hume–Rothery rules describing the conditions under which a metal could dissolve in another metal to form solid solution. The two elements have similar atomic radii, crystal structure, valence, and electronegativity so it expected the two metals form an ideal solid solution. At the nanoscale, Miyajima et al. proposed the replacement of electronegativity in the Hume–Rothery rules by one based on the molar heat of vaporization, which is related to the cohesive energy of the material [13,14]. In this work sublimation energy is used rather than heat of vaporization. Table 1 shows atomic radii and Pauling electronegativity for selected metals [15]. The surface energy of Co–Ni alloy nanoparticles at different mole fractions is shown in Fig. 1 calculated from the working Eq. (6). The surface energy values were very close and the inset shows the surface energies at the macroscopic scale when the number of atoms is in the range 10^3–10^5 to highlight the slight differences present. Previous work on the measurement of surface tensions of molten Co–Ni alloys experimentally showed little influence of changing the concentration of Co on the surface tension of Ni–Co alloys in the studied Co concentration range [16]. The weighted average value of surface energy at mole fraction of 0.5 Ni–0.5 Co has the value of 2161mJ/m^2 which is the same value obtained by applying Eq. (2). This means there is a slight tendency of surface segregation of one of the components to be expected in this alloy. Study of molten alloys of nickel with other metals including cobalt showed a slight segregation of cobalt inside the molten Co–Ni alloy [17]. The general trend is that the surface energy of alloy decreases with decreasing size (number of atoms in the nanoparticle) as can be seen in Fig. 1. The slight difference that exists in the value of the surface energy at the macroscopic scale (when the number of atoms is large), becomes negligible as the number of atoms becomes smaller which implies that the favorable segregation of the component with the lowest surface energy cannot be

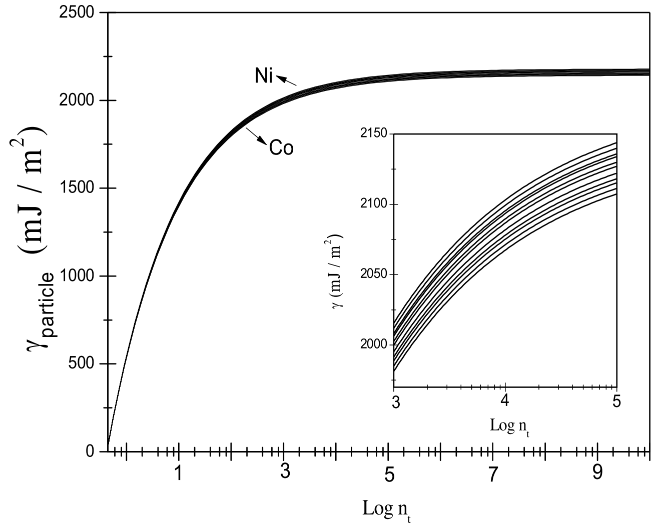

Fig. 1. Size dependent surface energy of Co – Ni alloy nanoparticles.

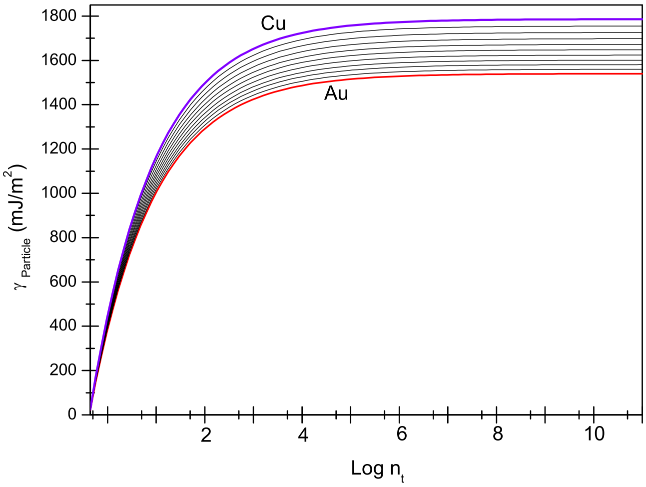

Fig. 2. Size dependent surface energy of Au – Cu alloy nanoparticles.

differentiated from that of the one with the slightly higher surface energy.

Surface energies of Au–Cu alloy, which fulfills three of the four Hume–Rothery rules namely atomic radii, crystal structure and valence, are shown in Fig. 2. The two metals are completely miscible in both solid and liquid phases [18–20]. As in the Co–Ni system all data merge to very close values when the particle size is about 100. The weighted average value of surface energy at mole fraction of 0.5 Au–0.5 Cu has the value 1663mJ/m^2 while the calculated value is given as 1648mJ/m^2. This is an indication that Au is segregated on the alloy surface. This result is confirmed by previous works which reported that gold in an Au–Cu alloy is the favorable component to segregate on the surface as it has the lower surface energy value [18]. The general trend is of course as that in the case of Co–Ni where the surface energy decreases with decreasing size. However due to higher sublimation energy of gold there is a considerable difference in the value of surface energy at the macroscopic scale when the number of atoms is large. This difference decreases with decreasing size and becomes negligible at a size of about five atoms. It is clear that the Co–Ni system has smaller differences in its surface energy values than the Au–Cu system.

In Fig. 3 the surface energy as a function of particle size of Cu–Li alloy of different compositions. This system represents deviation from the Hume–Rothery rules where the size differences of aluminum and copper elements in this binary alloy differ by about 15%. On such cases alloys are expected to exhibit either positive or negative deviation from Raoult's law. Positive deviations are usually attributed to size effect when the volume ratio of the constituent elements is larger than 2 while positive or negative deviations are related to heat of mixing and expected in systems in which there are large differences of electronegativity between metals [21–23]. Although the Cu–Li elements are expected to be soluble in one another, there is clearly a considerable difference at large particle size and small particle size (number of atoms ~220). Below 220 atoms one can say that the present difference at larger atom number between the surface energy values becomes negligible. One has to say that in this system solid-solution formation is not favorable according to Hume-Rothery rules due to the electronegativity difference [18]. However, nano-solid solution formation is possible below a particle size of 220 atoms as seen in Fig. 3. The surface tensions of liquid Al–Cu binary alloys at different compositions were investigated experimentally and theoretically and values were monotonically decreasing with the increase in aluminum concentration. Surface segregation of aluminum was also observed especially on the topmost monolayer [24].

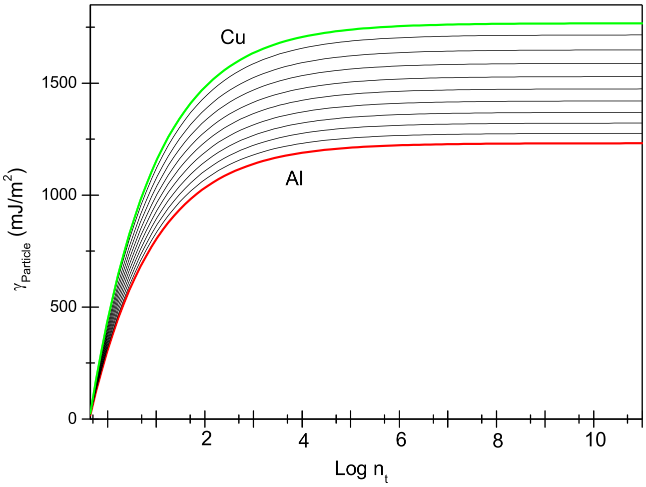

Fig. 3. Size dependent surface energy of Cu – Al alloy nanoparticles.

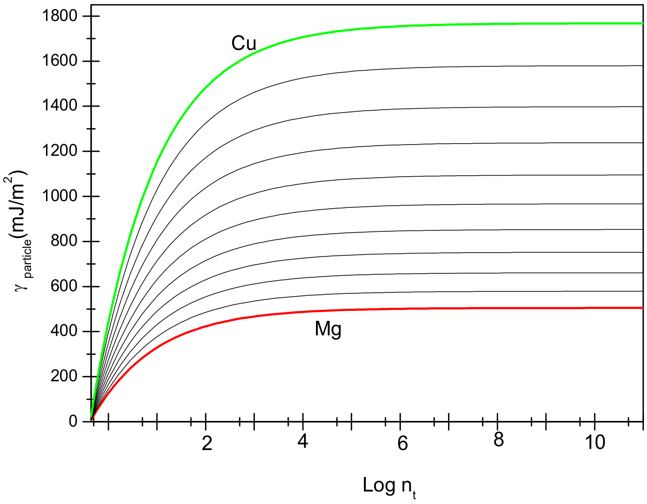

Fig. 4. Size dependent surface energy of Cu – Mg alloy nanoparticles.

In Figs. 4 and 5 plots of surface energy values versus particle size for the two alloys Cu–Mg and Mo–Cs are represented. These alloys are not favorable according Hume-Rothery rules due to size mismatch, and the difference in electronegativities of the constituent atoms is sufficiently large to cause phase separation. Copper and

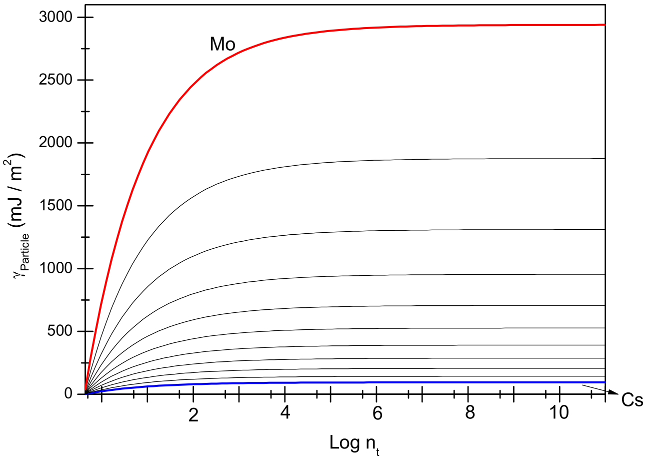

Fig. 5. Size dependent surface energy of Mo – Cs alloy nanoparticles.

magnesium are known to have limited solubility in one another and they form an amorphous phase rather than a solid solution [15,25]. This system displays much wider differences in the surface energy values upon increasing the Mg content both when the number of atoms is large and when it is small enough to be considered nano. However and according to our calculation they may form a nano-solid solution at a very small number of atoms ($\sim 6-7$ atoms). The differences in atomic sizes and electronegativities of molybdenum and cesium are so extreme to the extent that no previous work reported the formation of solid solutions from these two metals. This is technically due to the fact that the melting point of molybdenum is much higher than the boiling point of cesium which means that preparing such an alloy is not possible at the macroscopic scale. According to this work, mismatching between the two metals is intrinsic at both micro- and macroscopic levels to the extent that the formation of solid solution under any circumstances is prevented. However, the interesting finding here is that these two metals may form a nano-solid solution when the number of atoms in the nanoparticle is about 5–6 atoms. This may be achieved by evaporating the two metals separately to a substrate in such a way that the total number of atoms is about 6 atoms. Such finding has never been reported before and it is very interesting and challenging to the segment of the scientific community in question. From this relatively simple theoretical model it turned out to be that when solid solution formation is impossible at the macroscopic scale things are different at the nano scale and the feasibility of nano-solid solution formation is there. This simple finding here could have a fundamental as well as technical impact in the future. However, much more work is needed both theoretically and when possible experimentally.

4. Summary

We have extended our model to calculate the surface energy of metallic binary alloys and found that the surface energy decreases with decreasing particle size. The interesting and most attractive finding is that binary metals that obey Hume–Rothery rules have small difference in their surface energy values at macroscopic as well as the nano-scale and solid solution formation is favorable. When solid solution formation is not possible according to Hume–Rothery rules at the macroscopic scale, a nano-solid solution formation may be possible. This was demonstrated by $Co-Ni$, $Au-Cu$, $Cu-Al$, $Cu-Mg$ and in the extreme case by $Mo-Cs$ binary alloys. This is interesting and presents a challenge to the theoretical and technological segment of the scientific community in concern.

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