



Au-Ni nanoparticles: Phase diagram prediction, synthesis, characterization, and thermal stability



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ARTICLE INFO

Keywords:

Nanoalloy

CALPHAD

Phase diagram

Spinodal decomposition

ABSTRACT

The Au-Ni nanoparticles (NPs) were prepared by oleylamine solvothermal synthesis from metal precursors. The Au-Ni phase diagram prediction respecting the particle size was calculated by the CALPHAD method. The hydrodynamic size of the AuNi NPs in a nonpolar organic solvent was measured by the dynamic light scattering (DLS) method. The average hydrodynamic sizes of the nanoparticle samples were between 18 and 25 nm. The metallic composition of the AuNi NP samples was obtained by inductively-coupled plasma atomic emission spectroscopy (ICP-OES). The metallic fraction inside AuNi NPs was varied Au-(30–70) wt%Ni. The steric oleylamine stabilization was observed. The individual AuNi NPs were investigated by transmission electron microscopy (TEM). The dry nanopowder was also studied. The structures of the aggregated samples were investigated by scanning electron microscopy (SEM). The AuNi NPs reveal randomly mixed face-centered cubic (FCC) crystal lattices. The phase transformations were studied under inert gas and air. The samples were studied by differential scanning calorimetry (DSC).

1. Introduction

The behavior of the macro-sized alloy (bulk alloy) differs from a system of individual nano alloy particles (nanoalloy) despite that both bulk and nanoalloy have the same composition. The fundamental reasons are a high ratio between numbers of surface and volume atoms and the presence of the adsorbed or bonded molecules (ligands) on the nanoparticle surface. The main function of the ligands is to stabilize nanoparticles. The second function is to functionalize the nanoparticle surface for subsequent applications.

The AuNi nanoparticles could provide opportunities to combine properties of gold nanoparticles, which are considered as non-toxic and are intensively investigated now, in conjunction with magnetic properties of nickel atoms. These nanoparticles could be promising carriers for surface anchored agents in diagnostics, medicine, drug delivery, etc.

The phase behavior of the AuNi alloy in the macroscopic form (bulk) is well known. The stable phase diagram was clarified experimentally during the 20th century. The AuNi bulk alloy represents a non-ideal system with limited mutual miscibility of the metals in the solid state at low-temperature region [1].

At the beginning of this century (2005), Wang and colleagues performed a detailed thermodynamic assessment of the phases of the

AuNi system using the CALPHAD method [1]. The result of their work was the accurate phase diagram of the Au-Ni system, which reveals the critical point at 816 °C (Au-74 at%Ni) and the congruent point at 941 °C (Au-36 at%Ni). The accepted description of the phases of the AuNi system [1] is in accordance with the thermodynamic data, such as entropy and enthalpy of mixing, the activity of both gold and nickel in the AuNi bulk.

Despite the FCC lattice of pure Au and Ni, their alloy reveals decomposition to the Au-rich FCC phase (FCC_Au) and the Ni-rich FCC phase (FCC_Ni) at temperatures below the critical point. The thermodynamic equilibrium of the two phases (FCC_Au + FCC_Ni) is created by either discontinuous precipitation or by the spinodal decomposition of the supersaturated FCC AuNi alloy [2]. The spinodal decomposition occurs at a low-temperature range up to 250 °C. The discontinuous precipitation (nucleation and growth) takes place at high-temperature range (250–816) °C. The kinetics of both phase transformations is slow [2]. The earlier time of the start of the discontinuous precipitation is 250 s at 600 °C. The earlier time of the start of the spinodal decomposition is 1000 s at 150 °C. It appears that both kinds of the phase transformations are diffusion controlled. Rates of chemical diffusion of gold and nickel in the fcc AuNi bulk alloy can be obtained from diffusional mobilities of both gold and nickel [3].

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Irradiation-induced spinodal decomposition has been also observed in-situ on thin AuNi foil in an electron microscope with 0.4–1 MeV electron irradiation up to approx. 600 °C [4].

The properties of AuNi nanoparticles should be inferred from the properties of the bulk alloys but deviations caused by nanoscale particle size and by the presence of ligands on the surface were observed. The preparations of the AuNi nanoparticles was realized using physical methods and by routes of chemical synthesis. The products of these methods are different types of nanoparticles as core@shell, supersaturated AuNi NPs, and Janus NPs. The last type is a special type of nanoparticle, its surface has two or more distinct physical properties.

A simple physical technique for preparing of AuNi particles is a dewetting method [5,6]. The first step of the procedure is physical vapor deposition (PVD) of thin Au/Ni bilayer on a suitable substrate. The heating of the sample at temperatures in two phase region causes separation of the metal bilayer from the substrate surface and the formation of Janus Au/Ni bimetallic particles. Herz et al. [6] prepared by this way submicron particles that were formed by (FCC_Au + FCC_Ni) phases. It is possible to homogenize the particles if they are annealed at a high temperature in the FCC AuNi single phase region. Consequently, the formation of the FCC magnetic supersaturated AuNi particles is possible after cooling to ambient temperature [7]. The main disadvantage of the dewetting method is that particles below approx. 0.1 μm cannot be prepared.

Core@shell nanoparticles that consist of Au cores covered by Ni (Au@Ni) can be prepared by the metal gas condensation method [8]. The product has a huge magnetization generated by Faraday Induction. The magnetism is not lost even if the oxidation of the Au@Ni nanoparticles to particles containing NiO occurred.

The wet chemical synthesis of AuNi NPs is more promising than physical methods. The synthesis can use inorganic Ni²⁺ salts and tetrachloroauric acid. Sodium tetrahydroborate (NaBH₄) is often used as a reducing agent. Different electrochemical potentials of the gold and the less noble nickel adversely affect the reduction step. Therefore, it is easier to synthesize the core@shell nanoparticles (Au@Ni NPs) than to prepare nanoparticles with a homogeneous supersaturated composition (AuNi NPs). The Au@Ni NPs were prepared by Chiu et al. in 2009 [9] using a water-in-oil microemulsion. Also, other authors obtained similar products [10,11]. Alternatively, laser ablation of Ni target in Au colloidal solution can also be used for NP synthesis [12]. At these conditions, the formation of bimetallic Au@Ni NPs and complex NiO:Au nanoparticles occurred. The preparation of the Ni@Au nanoparticles (Ni in the center, shell enriched in Au!) that are stable at room temperature is also very interesting research that was done by Authen and a team in 2008 [13]. They obtained the magnetic Ni-Au nanoparticles of a small size (3 nm) using PAMAM (polyamidoamine) dendrimer and inorganic salts of Au and Ni.

The nanoparticles based on AuNi alloys are considered promising catalysts for chemical reactions [14]. For example aerobic oxidative esterification of aldehydes with alcohols [15], hydrogen generation by hydrolysis of basic NaBH₄ solutions [16], electrocatalyzed borohydride oxidation [11]. Fine nanoparticles of Ni on pNIPAM-coated Au nanoparticles can be used for the preparation of special sensors [17].

Generally, the nanoparticles consisting of gold and nickel are objects, which are discussed in theoretical and experimental nanoparticle research. The phenomenon of the phase separation of the supersaturated Au-Ni nanoparticle was theoretically investigated by the groups of Herz, Friák, and others [18] but the experimental preparation of the supersaturated AuNi nanoparticles represents a great challenge to the synthetic research.

2. Prediction of Au-Ni nanoalloy phase diagram

Phase diagram prediction of AuNi nanoalloys was performed using a similar method as presented by Lee and Park [19,20] and others [21,22]. The employed CALPHAD method [20] is based on the

minimization of the molar Gibbs energy of the phases present in the entire system. The Gibbs energy of the phase (liquid or FCC solid) that involve 1 mol of the individual nanoparticles is given by Eq. (1).

$$G^{Total} = G^{Bulk} + G^{Surface} \quad (1)$$

where G^{Bulk} is the Gibbs energies of the bulk binary phase expressed as Eq. (2).

$$G^{Bulk} = x_A G_A^o + x_B G_B^o + RT(x_A \ln x_A + x_B \ln x_B) + G^{Ex,Bulk} \quad (2)$$

x_A and x_B are mole fractions of A and B, G_A^o and G_B^o are the standard Gibbs energies of A and B, R is the universal gas constant, T is the temperature and $G^{Ex,Bulk}$ is the excess Gibbs energy of the bulk which is given by Eq. (3).

$$G^{Ex,Bulk} = x_A x_B \sum_v L^v(T)(x_B - x_A)^v \quad (3)$$

where index $v = 0, 1, 2, \dots$ in temperature dependent parameters

$$L^v(T) = a_v + b_v \cdot T + c_v \cdot T \cdot \ln(T)$$

The second term in Eq. (1) is the Gibbs energy of the surface of the nanoparticles $G^{Surface}$. This surface energy for isotropic spherical particles is expressed by

$$G^{Surface} = \frac{2C\sigma V}{r} \quad (4)$$

where C is a correction factor considering the effects from the shape of the surface strain due to nonuniformity, and the uncertainty of the surface tension measurements, estimated for a liquid to be 1.00 and for an fcc solid structure 1.05 [23], σ is the surface tension, r is the radius of the particle and V is the molar volume.

The molar volume for the binary system is expressed as the sum of fractions of each constituent (Eq. (5)).

$$V = x_A V_A + x_B V_B \quad (5)$$

For calculation of the surface tension of a binary liquid alloy the Butler equation [24] can be used expressed by

$$\begin{aligned} \sigma &= \sigma_A + \frac{1}{A_A} (G_A^{Surface} - G_A^{Ex,Bulk}) + \frac{RT}{A_A} \ln \left(\frac{1 - x_B^S}{1 - x_B} \right) \\ &= \sigma_B + \frac{1}{A_B} (G_B^{Surface} - G_B^{Ex,Bulk}) + \frac{RT}{A_B} \ln \left(\frac{x_B^S}{x_B} \right) \end{aligned} \quad (6)$$

where σ_A and σ_B are the surface tensions of pure species A and B, A_A and A_B are the superficial areas occupied by the liquid component A and B, $G_A^{Surface}$ and $G_B^{Surface}$ are the partial Gibbs energies of component A and B in the surface and $G_A^{Ex,Bulk}$, $G_B^{Ex,Bulk}$ are the partial Gibbs energies of component A and B in bulk.

The partial Gibbs energy $G_A^{Surface}$ of component A is presented as Eq. (7).

$$G_A^{Surface} = \beta^{mix} G^{Ex,Bulk} \quad (7)$$

where β^{mix} is a parameter corresponding to the ratio of the coordination number in the surface in the bulk and equal to β^{Pure} and the parameter is estimated to be 0.83 [25] and later on 0.85 [20].

The parameter β^{Pure} is determined from Eq. (8).

$$\sigma_A A_A = (1 - \beta^{Pure}) \Delta H_{LG,A} \quad (8)$$

where $\Delta H_{LG,A}$ is the heat for the liquid-gas transformation of metal A. A similar equation for solid β^{Pure} is given by Eq. (9).

$$\sigma_A A_A = (1 - \beta^{Pure}) \Delta H_{SG,A} \quad (9)$$

where $\Delta H_{SG,A}$ is the heat for solid-gas transformation of metal A.

The parameter β^{Pure} for solid state was estimated to be 0.84 [20], which is close to liquid metals. Accordingly, it is considered that the surface relaxation and rearrangement effects are almost the same for both liquid and solid metals. Therefore, if the differences in shape and surface strain with respect to composition are ignorable. According to

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