Prediction of atomic arrangement of Pt-Cu nanoalloy by genetic algorithm

J S Oh¹, H-S Nam², J-H Choi¹ and S-C Lee¹

¹Future Convergence Technology Research Division, Korea Institute of Science and Technology, Seoul, 136-791, Korea
²Center for Materials and Processes of Self-Assembly and School of Advanced Materials Engineering, Kookmin University, Seoul, 136-702, Korea

E-mail: leesc@kist.re.kr

Abstract. The prediction of atomic arrangements for a nanoalloy is of critical importance in developing a novel catalyst for clean energy applications because these arrangements determine the catalytic activities of a nanoalloy. So, the development of a reliable method for predicting atomic arrangements has become increasingly important. In this study, the atomic arrangements of the Pt-Cu in a truncated octahedron (TOh) shaped nanoalloy of various Pt-Cu compositions were predicted. We developed a genetic algorithm (GA) code to predict atomic arrangements, and this code was combined with classical molecular dynamics (MD) simulations to evaluate the optimality of each atomic arrangement. The GA calculation predicted a predominantly multilayered core-shell structure for the Pt-Cu nanoalloy, regardless of the Pt-Cu composition ratio. The cause of a multilayered core-shell structure in the Pt-Cu nanoalloy can be interpreted by the interaction between the intrinsic properties of Pt and Cu, such as their surface energies and miscibility.

1. Introduction

It has been widely accepted that platinum (Pt) is the best catalyst in many practical applications such as fuel cells, lithium-based batteries and etc. However, the limited amount of Pt reserves and the high cost of Pt have demanded the search for other materials having comparable catalytic activity of Pt. Since Pt cannot be completely replaced in current applications, the alloying of Pt with other metals has been widely studied. Reducing the Pt load and at the same time, maximizing the catalytic activity, Pt alloys have been synthesized as nanoparticles with sizes ranging from 3 to 5 nanometers in diameter. From these sizes, high surface-to-volume ratio can be achieved. Considering that the catalytic activity of a nanoparticle depends critically on the atomic configurations of its constituent metals, it is necessary to understand the atomic configurations of nanoparticles. Unfortunately, neither experimental nor single computational method is effective for observing the atomic configurations of nanoparticles with those sizes.

In this paper, we have approached the prediction of atomic arrangement in a fixed shape from the point of an optimization problem based on the genetic algorithm (GA). The atomic arrangement with the lowest total energy is regarded as the optimal arrangement, which is searched by an optimization method. For such a search, GA was adopted for its outstanding searching ability and generality [1]. In order to search for, or predict, the optimal atom arrangement, the ‘pyGA’ code written in Python language [2] was developed. It was then combined with the molecular dynamics (MD) code XMD [3] and the newly developed embedded atom method (EAM) potential to estimate the total energy of the designated atomic arrangement. With the pyGA, we successfully predicted the atomic arrangements of Pt-Cu nanoalloy in the truncated octahedron (TOh) shape with 1,654 atoms and observed their distinctive structural features in the predicted atomic arrangements regardless of the Pt-Cu composition.
2. Structural Features of Pt-Cu nanoalloy

The TOh has been known to be one of the most stable structures observed for an Face-Centered Cubic (FCC) based nanoalloy [4], and the FCC stacking sequence is preferred for nanoalloys larger than 3 nm in diameter [5,6]. An isotropic TOh nanoalloy with 1,654 atoms was constructed, which is approximately 3.5 nm in diameter [7].

Finding the optimal atomic arrangement of an A-B binary nanoalloy of a given TOh structure corresponds to finding an arrangement having the lowest total energy in the solution space, which contains all feasible atomic arrangements. The solution space size is defined as the number of feasible atomic arrangements of \(a:b\) composition for the binary nanoalloy, without consideration of the atomic symmetry in the nanoalloy. It is estimated based on the formula \(N!/(A!B!)\) [8], where \(A+B=N\), \(A\), \(B\) are the numbers of the corresponding atomic species in the compositional fraction \(a\), \(b\) and \(N\) is the total number of atoms in the nanoalloy. The solution space size of various compositions with 1,654 atoms are tabulated in the Table 1.

| Pt:Cu | Solution space size | Number of searching | Total energy [eV] |
|-------|---------------------|---------------------|-------------------|
| 1:3   | 1.13 \(\times\) 10\(^{672}\) | 1.4 \(\times\) 10\(^{6}\) | -6571.34 |
| 2:3   | 4.32 \(\times\) 10\(^{682}\) | 1.6 \(\times\) 10\(^{6}\) | -7156.00 |
| 1:1   | 1.57 \(\times\) 10\(^{697}\) | 2.0 \(\times\) 10\(^{6}\) | -7502.38 |
| 3:2   | 4.32 \(\times\) 10\(^{682}\) | 1.3 \(\times\) 10\(^{6}\) | -7835.75 |
| 3:1   | 1.13 \(\times\) 10\(^{672}\) | 1.5 \(\times\) 10\(^{6}\) | -8323.15 |

3. Calculation Methods

3.1. Genetic algorithm for the searching method

The GA is a very well known searching and optimization method based on the natural selection and survival of the fittest [9]. It mimics the biological evolution in the natural world. Following the basic concept of GA, pyGA was developed to predict the atomic arrangement in a bimetallic nanoalloy [7]. In pyGA, the total energy represented the optimality of an atomic arrangement in the solution space.

The input parameters of the pyGA code used in this study were as follows. The population size was 100 and the initial population was generated at random. The ‘Roulette Wheel’ selection operator and Partially Matched Crossover (PMX) [9] crossover operator were chosen. The probability of mutation was 0.0015. In order to pass down the dominant properties to the next generation, elitism was also implemented in pyGA. The stopping criterion was also prescribed like other input parameters. When a value of the lowest total energy had not changed in 1,000 consecutive generations, then pyGA terminated the evolution and regarded the atomic arrangement having the lowest total energy as the optimal one.

3.2. Molecular dynamics for the total energy calculation

For calculating the total energy of an atomic arrangement in the searching procedure, the MD simulation program XMD with the EAM potential was adopted. In order to include the effect of atomic position relaxation to yield a more realistic result, the conjugate gradient method was additionally implemented in the XMD. The analytic formula of EAM was originally proposed by A. Voter [10], but some parameters describing the inter-atomic interactions and thermodynamic properties were adjusted for this prediction [11]. The crucial properties of the nanoalloy, such as the surface energy, cohesive energy, miscibility, which is the heat of mixing, and the melting temperature were well reproduced by using the newly developed EAM potentials.

4. Results and Discussion

The search performances for the prediction at each composition were almost equivalent in spite of the variations in the composition. In the pyGA calculation, 10\(^6\) atomic arrangements were commonly searched to find the lowest energy configuration, which quantitatively equals 1.2 ~ 1.5 % of the solution space. This pyGA prediction required smaller number of searching than the Monte Carlo simulation [11]. Table 1 lists the number of searching to predict an atomic arrangement having the lowest total energy predicted from pyGA. The corresponding atomic arrangements are figured in Fig 1.
Figure 1. Predicted atomic arrangements in the Pt-Cu nanoalloy. (dark/blue : Pt, light/red : Cu) The first row shows the surface configurations, and the second row shows the cross sectional arrangements along the <010> direction.

Figure 2. The layered-shell structure in the TOh with 1,654 atoms.

Figure 3. Prediction of Pt fraction in the Pt-Cu nanoalloy according to layered-shell. The fraction of Pt show a zigzag pattern, which starts from the surface to the core.

Fig. 1 shows the predicted ones from the pyGA code according to composition. The upper and lower rows are snapshots of the surface and cross-sectional views, respectively. The proportion of atom species on the surface changed according to composition. At the composition ratio of Pt:Cu = 3:1, only Cu species existed all along the edges of the surface. At the composition ratio of 1:1, entire Cu {100} facets and Cu-rich {111} facets were predicted. However, at the composition ratios of 1:3 and 2:3 = Pt:Cu, no Pt atoms existed on the {100} facets or on the {111} facets. This indicated that on the surface, Cu occupied firstly on the edges, then on the {100} and {111} facets with increasing composition of Cu. This phenomenon can be interpreted by the difference of the surface energy as described in the EAM potential [11]. The relations between the surface energies of Pt and Cu is as follows: \( \text{Pt}\{100\} > \text{Cu}\{100\}, \frac{\text{Cu}\{100\}/\text{Pt}\{100\}}{0.76} \) and \( \text{Pt}\{111\} > \text{Cu}\{111\}, \frac{\text{Cu}\{111\}/\text{Pt}\{111\}}{0.80} \). Due to the smallest coordination number on the edges in the FCC shape, the atoms on the edges are greatly influenced by the surface energy. Therefore, preoccupancy of Cu on the edges is explained by the lower surface energies of both Cu {100} and {111} facets. Consequently, the Cu species is regarded as the dominant atom species on the overall surface.

For the further analysis, TOh with 1,654 atoms was divided into 7 layered-shells like an onion, as partially shown in the Fig. 2. The fraction of Pt in each layered-shell was calculated and drawn in a graphical form in Fig. 3. The fraction of Pt drastically oscillated along the x-axis in all composition ratios. Analyzing the oscillation tendency from Fig. 3, it was concluded that the Pt-Cu nanoalloy had a remarkable structural feature that of an onion-like multilayered core-shell with a Cu dominant surface for all composition ratios. But closer to the core, the onion-like multilayered core-shell structure lost its form. Considering the relatively smaller number of atoms on the inner shells than on the surface or subsurface, the structural tendency appeared to be stronger on the outer layered-shells than on the inner shells.
5. Conclusions
Atomic arrangements of Pt-Cu nanoalloy according to various Pt:Cu composition ratios were predicted by using the GA and MD combined calculations. We developed the pyGA code written in Python language. The combined simulation predicted an onion-like multilayered core-shell structure of TOh Pt-Cu nanoalloy with 1,654 atoms, regardless of the composition ratio. This core-shell structure resulted from the surface energies and heat of mixing of Pt and Cu. In further studies, bulk alloy structure will be compared with nanoalloy structure to obtain more details and to understand the relations between size and morphology.

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