Computer simulation of dealloying in Cu-Pt nanoparticles

N Yu Sdobnyakov, V M Samsonov, A Yu Kolosov, V S Myasnichenko, K G Savina, S A Vasilyev, P M Ershov, R E Grigoryev, S S Bogdanov and D N Sokolov

Tver State University, 170100, Russia, Tver, 33, Zhelyabova str.

E-mail: nsdobnyakov@mail.ru

Abstract. Two basic alternative atomistic simulation methods (molecular dynamics and Monte-Carlo) have been used to reproduce the dealloying phenomenon in Cu-Pt nanoalloys. Using the Gupta (tight-binding) potential, we simulated nanoparticles consisting initially of 1500 Cu and 1500 Pt atoms. The involved programs propose search and following removing Cu atoms with the lowest specific binding energies. We have found that as a result of dealloying the particle surface layer is really enriched with Pt atoms. However the particle core keeps in general the structure of the initial nanoalloy. This effect is especially noticeable in molecular dynamics simulation. We have also established that dealloying results in formation of a defected particle structure (vacancies, first of all). Presumably, just such an effect yields the porous structure of bigger Cu-Pt particles in laboratory experiments on dealloying.

1. Introduction

The study of binary metal nanoclusters is of particular interest for scientists as such nanoclusters demonstrate a number of specific phenomena in comparison with their monometallic analogs of the same size, e.g. segregation of one of the particle components. Controlling the size, composition, structure and degree of chemical ordering (including degree of mixing or segregation of constituent metals), it is possible to control the physicochemical properties of some new nanomaterials promising for industrial applications [1, 2]. Pt-based nanoparticles are of interest because of their higher reactivity with organic molecules, which makes them to be useful for electrocatalysis in fuel cells. Alloys of Pt, as well as of other transition metals, such as Fe, Co, Ni and Cu, have been widely studied and their properties optimized for more than two decades that results in a significant increase in their activity in comparison with monometallic materials. The results of these studies indicate that Pt-Cu nanosized alloys are easily synthesized using some methods that allow to adjust the particle size and shape. Under certain conditions, the surface of these alloys is usually subjected to a process known as dealloying or selective corrosion. As a result of this process, one of the particle components, e.g. the less noble metal, dissolves from the outermost atomic layers [3]. Thus, this process can be used to produce Pt-Cu nanoparticles with the necessary structure. So in [4] the active phase of catalysts based on Pt alloy nanoparticles was obtained by electrochemical dissolution of the surface Cu atoms from a copper-rich Pt-Cu alloys. The structural and compositional investigations suggest that the purified active phase of the catalyst consists of a core-shell structure in which a multilayer shell with a higher Pt content surrounds the core of the particle with a lower Pt content.

The method of electrochemical dealloying is widely used to obtain bimetallic nanoparticles based on Pt. For example, in [5], two types of electrochemical methods were used on ordered intermetallic Cu$_3$Pt/C nanoparticles: the potential cyclic and potential static. The particle morphology was
significantly changed due to the surface rearrangement with a fast cycling of the scanning potential, and a Pt rich shell was noticeable on the surface. In the second experiment, a small fraction of particles, especially of relatively large ones, formed the porous structures. Therefore, the method under consideration allows one to obtain porous structures from sufficiently large bimetallic nanoparticles. This conclusion was verified in [6] where, using electrochemical dealloying of Pt-Cu alloy plates, the nanoporous platinum and platinum nanoparticles were obtained. In [7] it was found that removal of Cu from nanoparticles of the Pt-Cu binary alloy yielded some very active catalysts for the oxygen reduction reactions. Scientists are studying voltammetric profiles of the dissolution of Cu in the early stages of the process of the dealloying, which correlate to the synthesis conditions and the phase characteristics of nanoalloys with different Cu contents.

Determining a relationship between the particle size and the nanostructure of homogeneous bimetallic nanoparticles is important for development of technologies of the controlled synthesis of these nanomaterials. Despite the existence of experimental data on the dealloying, a number of open questions remain regarding this phenomenon. In particular, it remains unclear how to refine and stabilize these structures, why the porous structure formation takes place with increasing the particle size only. In this paper, an attempt is made to answer the above and other questions related to the dealloying in Cu-Pt nanoparticles. For this purpose, atomistic simulation involving two alternative methods (molecular dynamic and Monte Carlo) was used. Earlier [8] regulations of the dealloying in the Au-Ag systems were studied by employing an analogous combined approach.

2. Simulation technique

To solve the stated above problems, we have employed two independently developed computer programs based on the isothermal molecular dynamics (MD) and the Monte Carlo (MC) methods. In both cases, the interatomic interaction was described by the Gupta many-body potential [9] with parameterization [10]. For the cross-interactions, the modified Lorentz-Berthelot rule was used, i.e. the energy parameter was found as the geometric mean of the corresponding parameters of both components, and the spatial (linear) parameter as the arithmetic mean (table 1). The Nose-Hoover thermostat was used in the MD program. The MC program is based on the Metropolis scheme [11]. Our programs used for MD and MC simulations were tested by us on both simulation of the selective corrosion [8] and on investigation of the structural and thermodynamic characteristics of mono- and binary particles [12–14].

The initial configurations of the Cu-Pt nanoparticles contained 1500 Cu and 1500 Pt atoms. In the initial configurations, the Cu and Pt atoms were distributed uniformly throughout the particle volume. To simulate the dealloying, Cu atoms were gradually removed until half of the Cu atoms were left. After the removal process, the nanoparticle was relaxed. Thus, to a certain approximation, the two stages of the dealloying process noted in [5] were reproduced: 1) primary dealloying corresponding to the selective removal of Cu atoms from the nanoalloy; 2) secondary dealloying.

Table 1. Parameters of the Gupta potential.

| Metal  | $A$, eV | $\zeta$, eV | $\rho$ | $q$ | $r_0$, Å |
|--------|---------|-------------|--------|-----|---------|
| Pt-Pt  | 0.2975  | 2.695       | 10.612 | 4.004 | 2.775   |
| Cu-Cu  | 0.0855  | 1.224       | 10.960 | 2.278 | 2.556   |
| Cu-Pt  | 0.1595  | 1.816       | 10.786 | 3.141 | 2.6655  |

3. Results of simulation

Configurations presented in tables 2 and 3 (obtained employing the well-known program OVITO [16]) show evolution of the core phases in the Cu-Pt systems and of the energy spectra during the dealloying. In figures 1 and 2 the dependences are presented of the specific potential (cohesive) energy of atoms in the Cu-Pt nanoclusters on the coordination number obtained by using two alternative (MD and MC) methods. Comparison of these dependences shows that the MD structures have a higher density
in comparison with MC results. Besides, the components in MD configurations are characterized by higher coordination numbers (the graph in figure 2 is shifted to the right). At the same time, two alternative methods predict the same width of the energy variation range.

**Table 2.** Comparison of MD and MC instant configurations of the Cu-Pt systems of different sizes.

| Number of atoms | MC | The range of the potential energy, eV/atom | MD |
|-----------------|----|------------------------------------------|----|
| 3000            |    | -2.8527                                  |    |
| 2850            |    | -2.8527                                  |    |
| 2700            |    | -5.7301                                  |    |
| 2550            |    | -5.7301                                  |    |
| 2400            |    | -5.7301                                  |    |
Table 3. Core phases in the Cu-Pt systems. The green color marks the local fcc structure, the red color atoms corresponding to the hcp structure, the blue one to the bcc structure.

| Number of atoms | MC | MD |
|-----------------|----|----|
| 2250            | ![Image](image1.png) | ![Image](image2.png) |
| 2100            | ![Image](image3.png) | ![Image](image4.png) |
| 1950            | ![Image](image5.png) | ![Image](image6.png) |
In figure 3 the dependences of the specific potential energy on the number of atoms deleted from the particle $N_{del}$ are shown. Both dependences are close to linear, but shifted relative to each other by about 0.25 eV, although they are characterized by the same slope.

**Figure 1.** MC dependence of the specific potential energy of atoms in the Cu$_{1754}$-Pt$_{1496}$ nanocluster on the coordination number (CN).

**Figure 2.** MD dependence of the specific potential energy of atoms in the Cu$_{1751}$-Pt$_{1499}$ nanocluster on the coordination number.

**Figure 3.** Variation of the specific potential energy of Cu-Pt nanoclusters during the dealloying.

4. **Conclusion**

Thus, two different computer simulation algorithms adequately reproduce the process of the dealloying in binary Cu-Pt nanoparticles. In our opinion, some interesting results have been obtained that clarify the regularities of this process. In particular, it has been shown that dealloying should not noticeably
change the composition of the central part of the particle (the particle core), and the core partly keeps the initial structure of the binary nanoalloy. At the same time, with the removal of the Cu atoms, the degree of defectiveness of the particle increases as a result of a significant change of the surface most subjected to the dealloying. Apparently, it is the main factor resulting in the porosity of larger particles during the dealloying in laboratory experiments. In some cases, for example, when using nanoparticles as catalysts, the porosity can be a desirable factor, i.e. the dealloying can be recommended as a method for producing binary porous nanoparticles with the surface layers enriched by one of the metals.

Acknowledgments
This work was supported in part by the Russian Foundation for Basic Research (projects no. 18-03-00132-a, 20-37-70007, 20-33-90192) and by the Ministry of Science and Higher Education of the Russian Federation in the framework of the State Program in the Field of the Research Activity (project no. 0817-2020-0007).

References
[1] Guerrero-Jordan J, Cabellos J L, Johnston R L and Posada-Amarillas A 2018 Eur. Phys. J. B 91 123
[2] Khanal S, Spitale A, Bhattarai N, Bahena D, Velazquez-Salazar J J, Mejia-Rosales S, Mariscal M M and José-Yacaman M 2014 Nanotechnology 5 1371
[3] Malarcred P, Casalongue H G S, Masini F, Kaya S, Hernández-Fernández P, Deiana D, Ogasawara H, Stephens I E L, Nilsson A and Chorkendorff I 2015 Phys. Chem. Chem. Phys. 17 28121
[4] Mani P, Srivastava R, Strasser P 2008 J. Phys. Chem. C 112 2770
[5] Wang D L, Yu Y C, Zhu J, Liu S, Muller D A and Abruña H D 2015 Nano Lett. 15 1343
[6] Maruya K, Yamauchi R, Narushima T, Miura S and Yonezawa T 2013 J. Nanosci. Nanotech. 13 2999
[7] Strasser P, Koh S and Greeley J 2008 Phys. Chem. Chem. Phys. 10 3670
[8] Myasnichenko V S, Samsonov V M, Sdobnyakov N Yu, Bembel A G, Vasilyev S A, Kolosov A Yu, Savina K G, Ershov P M and Sokolov D N 2019 Physical and chemical aspects of the study of clusters, nanostructures and nanomaterials 11 487 [In Russian]
[9] Gupta R P 1981 Phys. Rev. B 23 6265
[10] Cleri F and Rosato V 1993 Phys. Rev. B 48 22
[11] Metropolis N and Ulam S 1949 J. Amer. Statist. Ass. 44 335
[12] Samsonov V M, Sdobnyakov N Yu, Myasnichenko V S, Talyzin I V, Kulagin V V, Vasilyev S A, Bembel A G, Kartoshkin A Yu and Sokolov D N 2018 J. Synch. Investig. 12 1206
[13] Samsonov V M, Sdobnyakov N Yu, Talyzin I V, Sokolov D N, Myasnichenko V S, Vasilyev S A and Kolosov A Yu 2019 J. Synch. Investig. 13 1185
[14] Kolosov A Yu, Sokolov D N, Sdobnyakov N Yu, Komarov P V, Bogdanov S S, Bogatov A A and Myasnichenko V S 2017 J. Nano- Electr. Phys. 9 05042
[15] Ye X-L, Lu N, Li X-J, Du K, Tan J and Jin H-J 2014 J. Electrochem. Soc. 161 C517
[16] Stukowski A 2010 Modell. Simul. Mater. Sci. Engin. 18 015012