Monte Carlo Simulation of Surface De-alloying of Au/Ni(110)

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Abstract

Based on BFS model and using Monte Carlo simulation we confirms the de-alloying in immiscible Au/Ni(110) system, and the critical Au coverage when de-alloying happens is also consistent with experiments. At the same time our simulation show that the structural phase transition will lead to the saturation of the number of alloying Au atoms. PACS: 68.18.Fg, 68.35.Dv, 68.35.Ct, 68.55.Ac
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I. Introduction

The surface alloy is an important phenomenon in hetero-growth of surface[1, 2, 3, 4]. By the observations of Scanning Tunneling Microscopy (STM) , gold atoms mix with copper atoms and form the Au-Cu $c(2 \times 2)$ structure for Au/Cu(110) system[5]; gold atoms mix with the silver atoms at next atomic layer below surface layer for Au/Ag(110)[6]. Theoretically, the equilibrium structures of surface alloy can be obtained by the calculation of total energy[7, 8]. The surface alloy of immiscible system, such as Au/Ni(110)[9], (Na,K)/Al(111)[10, 12, 11, 13], Ag/Pt(111)[14], Sb/Ag(111)[15], is an astonishing phenomenon because it is difficult to mix different kind atoms in bulk for these systems. Thus, we can compound some new and novel compounds on surface which are difficult to compound in bulk material. A few theoretical models have been presented to explain the surafce alloy in immiscible systems

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such as Effective-Medium Theory(EMT)[9], Tersoff Theory[16] and BFS Theory [17, 18]. Especially BFS model[17, 18, 28] have been successfully used to study the phenomenon of surface alloy especially in immiscible systems [29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39].

Recent experiment [19] for Au/Ni(110) system have shown that when coverage of deposited Au atom is above 0.4ML a new phenomenon "de-alloying" happen. Au atoms having already alloyed segregate again and form complex one-dimension chain perpendicular to closed-packed direction. A density function calculation have shown the interesting properties of these one -dimension chain[20]. In this work, using Monte Carlo simulation we study the de-alloying of Au/Ni(110) system, our results show that when coverage of Au atoms increase to above 0.40ML, the de-alloying occurs, which is consistent with experiment. Before present our results, we introduce the BFS model.

In this work we study the alloying and de-alloying of Au/Ni(110). Generally Au atoms are immiscible in Ni crystal. The experimental finding of Au atoms alloying to Ni(110) surface inspired the interests of immiscible systems. Based on BFS model, several theoretical calculations and computer simulations haven been explained the experimental phenomenon of the alloying. In this work we find that not only the alloying , BFS model can also successfully explain the de-alloying of Au/Ni(110).

II. BFS Model and Monte Carlo Methods

The BFS model is the generalization of Equivalent Crystal Theory(ECT)[21, 22] based on the ideas the formation of defects in perfect crystal equivalent to the changes of lattice constant. If the lattice constant of equilibrium perfect crystal is a_0, ECT theory requires there exist an equivalent lattice with lattice constant $a \neq a_0$ whose energy is equal to the the energy of the deformed lattice (the crystal after forming defects). The energy of equivalent lattice can calculate simply from the universal energy relation[23, 24, 25, 26] in terms of the change of lattice constant which is obtain from ECT equation.

The BFS model generalizes the ECT theory to alloy system, that is, including the chemical effects. The change of chemical environment is also equivalent to the change of lattice constant and the corresponding energy can calculate following the same as steps as the calculation of energy related to defects in crystal. Below, we give the main formulism of BFS model, more details review can be found in Ref.[28].

The formation energy of arbitrary alloy structure is the superposition of individual contributions ε_i, of nonequivalent atoms in the alloy,

$$\Delta H \quad = \quad \sum_i \varepsilon_i^S + g_i \varepsilon_i^{chem} \tag{1}$$

ε_i^S is the strain energy, ε_i^{chem} is chemical energy, g_i is the coupled parameter. The strain energy is calculated from

$$\varepsilon_i^S = E_C^i F^*(a_i^{S*}), \tag{2}$$

especially $F^*(a^*) = 1 - (1 + a^*)e^{-a^*}$ is an universal scaling function. $a_i^{S*} = q\frac{a_i^S - a_e^i}{l_i}$ is the scaled change of lattice constant, a_i^S is the lattice constant of equivalent crystal, a_e^i lattice constant for perfect lattice. The q, l are the parameters related structure and properties of system [21]. The coupling constant is $g_i = e^{-a_i^{S*}}$. The lattice constant of equivalent crystal a_i^S can obtained from the ECT equation

$$NR_1^p e^{-\alpha R_1} + MR_2^p e^{-[\alpha+(1/\lambda)]R_2} = \sum_j r_j^p e^{-[\alpha+S(r_j)]r_j} \tag{3}$$

$R_1(R_2)$ are the distances of first nearest(next nearest) neighbor of atom i, $N(M)$ is the atomic numbers of nearest(next nearest) neighbor. p, α, λ are the screening parameters defined in Ref[21, 30]. $S(r_1) = 0$ for nearest neighbor and $S(r_2) = 1/\lambda$ for next nearest neighbor.

Each of atoms in alloy has its own equivalent crystal, whose lattice constant which is dependent on the environment of the atom. In calculation of strain energy ε_i^S the structural effects are considered and chemical effects are ignored , that is, all atoms near by atom i identify as the same kind of atom as atom i. However chemical effects are included in part of chemical energy of BFS model ε_i^{chem} in which structural effects are ignored. The calculations of chemical energy are similar to strain energy, it ECT equation for atom i is

$$\begin{aligned} & NR_1^{p_i} e^{-\alpha_i R_1} + MR_2^{p_i} e^{-[\alpha_i+(1/\lambda_i)]R_2} \\ = & \sum_k r_1^{p_i} e^{-\alpha_{ik} r_1} + \sum_k r_2^{p_i} e^{-[\alpha_{ik}+(1/\lambda_i)]r_1} \end{aligned} \tag{4}$$

compared with Eq.3, only difference is the appearance of parameter $\alpha_{ik} = \alpha_{ik} + \Delta_{ki}$ for atom i which dependent on the kind of its nearby atoms k, if atom k is identical atom i, $\Delta_{ik} = \Delta_{ii} = 0$, otherwise, $\alpha_{ik} \neq 0$ which is just the chemical effect. In BFS model, the chemical energy includes only the chemical environment and ignores the structural facts, thus, r_1, r_2 is the nearest and next nearest distance of equilibrium crystal of atom i and retain the chemical environments of atom i. If we have solved the ECT equation, the chemical energy can calculate according to $\varepsilon_i^{chem} = \varepsilon_i^C - \varepsilon_i^{C0}$. The ε_i^{C0} is the energy without chemical impurities($\Delta_{ik} = 0$). The calculations of ε_i^C and ε_i^{C0} are summarized as below

$$\varepsilon_i^C = \gamma E_C^i F^*(a_i^{C*}) \qquad\qquad \varepsilon_{0_i}^C = \gamma_0 E_C^i F^*(a_i^{C0*}) \tag{5}$$

$$a_i^{C*} = \frac{q(a_i^C - a_i^e)}{l_i} \qquad\qquad a_i^{C0} = \frac{q(a_i^{C0} - a_i^e)}{l_i} \tag{6}$$

$$\gamma = \begin{cases} 1 & a_i^{C*} \geq 0 \\ -1 & a_i^{C*} < 0 \end{cases} \quad and \quad \gamma_0 = \begin{cases} 1 & a_i^{C0*} \geq 0 \\ -1 & a_i^{C0*} < 0 \end{cases} \tag{7}$$

We have used Monte Carlo Methods to simulate the surface alloying and de-alloying based on the BFS model. In simulation, we calculate energy for every configurations when sampling phase space of the system you are studying. Reject or accept of a configuration is based on Metropolis rule[27]. The key of Monte carlo simulation is the calculation of total energy. For BFS model, $\Delta H = \sum_i \varepsilon_i$. ε_i is dependent on the environment of atom i. If we consider a perfect lattice only includes one kind of atoms, the environment of atom i is the nearby configurations of atom i and is written as (n_i, m_i), $n_i(m_i)$ is the atomic number of nearest (next nearest) neighbor of atom i. So $\Delta H = \sum_i \varepsilon(n_i, m_i)$. Because we only consider the nearest and next nearest neighbor of an atom, the possible configurations are very limited for typical crystal (fcc,bcc,hcp and diamond structure), such as for fcc metal the number is 91. All configurations for every atoms are casted into this group of the 91 configurations. If having calculated energies of the 91 configurations before entering the main loop of Monte Carlo, in the main loop we only need to find which one in 91 configurations is corresponding to the current configuration. The total energy can calculate from above formulism. So we calculate energies only 91 times in our simulation. Exactly defining nearby configurations for every atoms is the main task in our simulation. For alloy system, the available nearby configurations are large, but every configurations only calculates one times, Monte carlo simulation is also fast. In our simulation, atoms move on 3D lattice. The atom i jump from site m to n, if the site n is empty, the atom i occupies the site n. If the site n has been occupied by another atom j with the different kind of atom i, the atom i exchanges position with atom j or the jump is rejected.

III. Results and Discussion

Based on BFS model, we simulated the dynamics of alloying Au/Ni(110). The simulation cell includes 5 atomic layers, and each layer contains 280 atom. The atomic number of substrate of the cell is 1400. We generally deposited Au atoms with coverage from 0 to 1ML or from 0 to 280 Au atoms in order to study the alloying and de-alloying of Au/Ni(110) system. Two atomic layers at bottom are fixed, periodical boundary are applied to the directions paralleling to surface. In our simulation, the direct exchanging of different kind of atom are allowed if an atom moves to the site already occupied by a different kind of atom. The sweep number of Monte carlo simulation is 50000 or 100000.

Fig. 1 shows the formation energy when an Au atom substitutes Ni atom in different layers. Left Panel shows the Au atom substitutes Ni atom in the surface layer. From this figure we find that it has the lowest formation energy when Au atom substitutes Ni atom of surface layer.Our results also indicate that Au atoms can't alloy into the Ni crystal which is the proof of immiscibility of Au/Ni system. The same result, that is, surface alloying of immiscible system, haven been report by other authors [18].

Fig. 2 shows the surface structure at low Au coverage at room temperature 300K. Fig. 2(a) shows the relaxed surface structure at 0.036 ML Au coverage. We find from this figure that all Au atoms are alloying into the surface layer except an Au atom is still on

the surface. The Ni atoms on surface, which are substituted by alloying Au atoms, form two Ni chains of 4 Ni atoms. The remained Au atom on surface forms an alloying dimer with a Ni atom. By increasing Au coverage to 0.1ML, the length of Ni chains also increase with increasing of number of alloying Au atoms. Alloying atomic chains also appear, and their lengths also increase. This is because the more Au atoms alloy into surface, and more substituted Ni atoms are jumped onto surface. Some of Au atoms, which have no time ally into surface layer, form the alloying chains with Ni atoms. The chance of forming alloying chain is larger than that of the lower coverage Fig. 2(a). Our results are in close agreement with experimental observations. An important difference compared with experiments is the smaller numbers of Ni dimer alloying into surface layer, on the contrary, in the experiments, most of Ni atoms are paired.

In the experiment at higher Au coverage, the de-alloying phenomenon is found with increasing Au coverage to 0.40ML[19]. The number of alloying Au atoms doesn't increase, on the contrary, decrease with increasing Au coverage. On the surface, one-dimension Ni chains with complicated structure perpendicular to closed packed direction are found. We study the change of surface structure throughly from low coverage to high coverage. The Monte Carlo simulations sweep 100000 times for each coverage, temperature is 300K. The results are shown in Fig. 3. From this figure we find the numbers of Au atoms alloying into surface layer decreases if the Au coverage increases continuously above 0.4ML. Our results are consistent with the experimental observation. The critical coverage characterized the de-alloying is exactly 0.40, the experimental value. From Fig. 3 we also find the number of Ni atoms on surface is larger than the number of alloying Au atoms when Au coverage is lesser than the critical value, which indicates that there are vacancy on the surface at low Au coverage. If n Ni atoms jump from prefect surface layer onto surface, n vacancies (unoccupied sites) will leave in surface layer; If m Au atoms alloy into the surface layer and occupy m unoccupied sites, the number of vacancies in surface layer will decrease and equal to $n - m$. If $n = m$, all sites in surface layer are occupied and no vacancies are in surface layer. When the de-alloying happens, some of Au atoms return to surface and at the same time some of Ni atom return to surface layer. From the figure, we also find the number of Ni atoms on surface is equal to the number of Au atoms of alloying surface layer. This means that an Au atom only substitutes a Ni atom and all the sites of surface layer are occupied without vacancy.

Fig. 4(a) gives the equilibrium structure at 0.4ML Au coverage after Monte Carlo relaxation 100000 steps. The Fig. 4(b) is the surface structure when we deposited randomly another 0.40ML Au on the already relaxed surface (Fig. 4(a)). Now we use the Fig. 4(b) (with coverage 0.8ML) as the new initial structure and relax another 100000 Monte Carlo steps. The structure Fig. 4(b) is unstable and relax to another equilibrium structure. We find, in the final surface structure, most of Au atoms return to surface. Only small part of Au atoms is inserted the alloying surface layer. Fig. 5 shows the change of the number of Au atoms alloying to surface layer with Monte Carlo steps. We find the number decreases rapidly and is approached to equilibrium value within only 100 Monte Carlo steps.

Generally at higher temperature the motion of atoms is faster, an atom has more chance to exchange with other atoms. Thus we expect that the degree of alloying will increase with temperature. We study the temperature effects of surface alloy using a larger cell which includes 5 atomic layers and contains 1120 Ni atoms for each atomic layer. We also deposited randomly 450 Au atoms on the surface. The total number of atoms in the cell is 6050. Fig. 6 shows the change of the number of Au atoms alloying into surface layer and the change of the number of Ni atoms on surface. we find the number of alloying Au atom increases with increasing temperature until temperature above 800K it is approach to saturation.

From Fig. 6 we can find the number of Ni atoms on surface almost increases simultaneously with the increasing of the number of alloying Au atoms when temperature is below 800K. When temperature above 800K the number of Ni atoms on surface also increases linearly at the same time the number of Alloying Au atoms approaches to saturation. The figure shows that the number of Ni atoms on surface is generally larger than the number of alloying Au atoms, the difference becames larger when temperature increases above 800K. This is indicated that a change of surface structure. The number of vacancy increases when temperature above 800K. The decrease of proportion of Ni atoms of substrate (surface layer) leads to the decrease of the chance of exchanging with Au atoms on surface, which prevents the increase of the number of alloying Au atoms. The structural change of surface is the direct reason of the saturation of the number of alloying Au atoms when temperature increases above 800K. The argument is confirmed by following simulation of pure Ni(110) surface. With increasing temperature, some Ni atoms will jump onto surface because of the thermal motion of atoms. When temperature above a critical temperature the surface will undergo a structural change or structural phase transition. The change of number of Ni atoms on surface is shown in Fig. 6 too. We find when temperature increase to about 900K the number of Ni atoms on surface increases abruptly from about 190 to 350. The jump of the number of Ni atoms on surface indicates the structural change of surface. The transition temperature 900K is close to the temperature when the number of alloying Au atoms approach to saturation.

IV. Conclusion

In conclusion, our Monte Carlo simulation confirms the de-alloying in immiscible Au/Ni(110) system, and the critical Au coverage when de-alloying happens is also consistent with experiments. At the same time our simulation shows that the structural phase transition will lead to the saturation of the number of alloying Au atoms. Experimentally, the Au atoms of alloying into surface layer are generally paired at low coverage but in our simulation most of Au atoms are single. This is indicated that the BFS model need to improve to explained more the surface phenomena.

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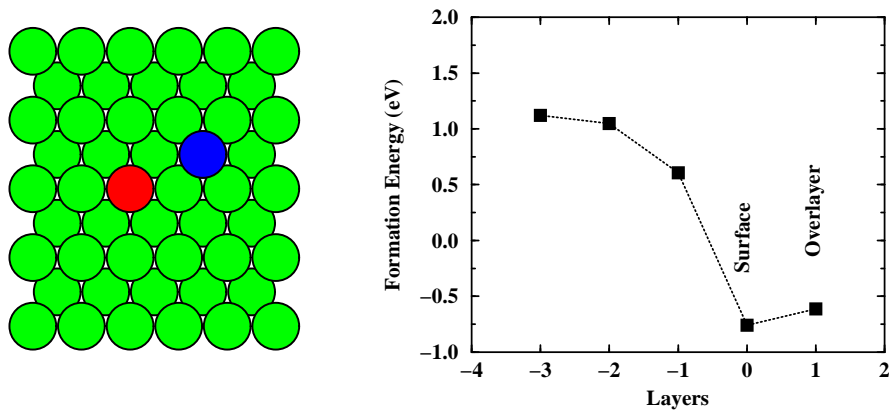
Figure 1: Formation Energy of an Au atom absorbed on surface or substituted other Ni atom in surface atomic layer or atomic layer below surface. (0). surface layer; (1) overlayer; (-1),(-2),(-3) and (-4) one,two,three and four below the surface. The Red ball is the alloying Au atom, Blue Ball Ni atom substituted by Au, Green ball is the substrate Ni atom
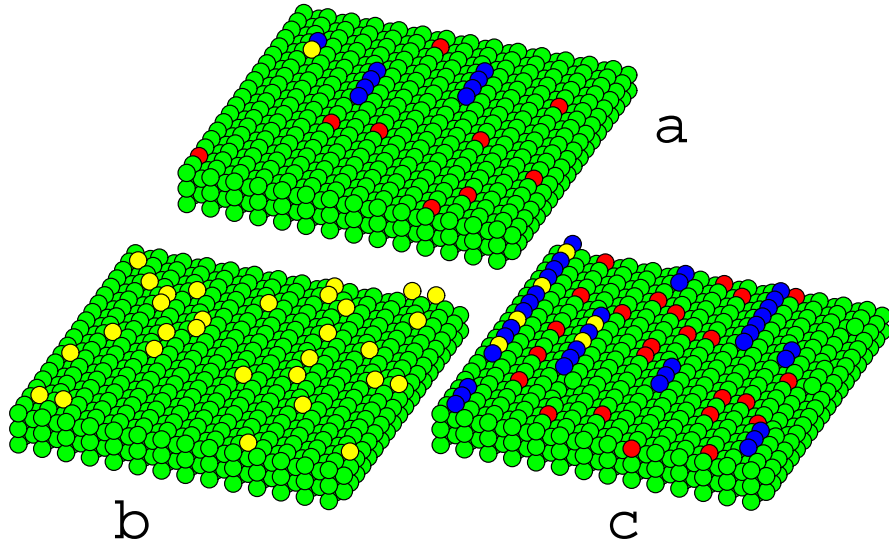
Figure 2: Surface structure at low coverage. (a) 0.036ML;(b) Initial Configuration at 0.1(ML);(3) Final Configuration at 0.3ML. (Green Ball) Ni atoms at or below surface layer; (Blue Ball) Ni atoms on surface (Overlayer); (Red Ball) Au atoms alloying to surface layer; (Yellow Ball) Au atoms on surface (Overlayer). Temperature set to 300K
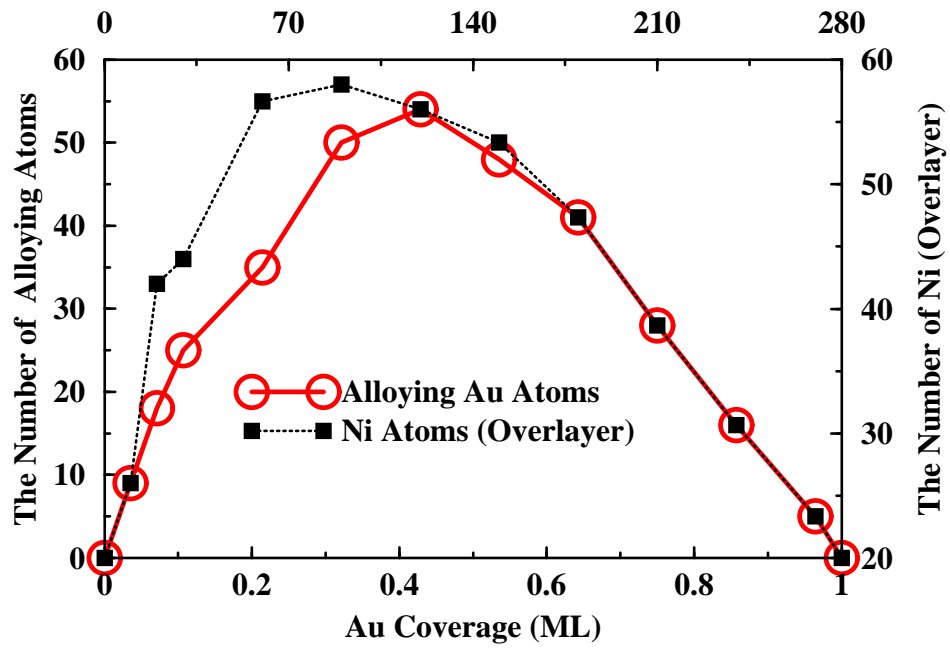
Figure 3: The changes of the number Au atoms alloying to surface (Red line) and the change of the number Ni atoms on surface formed due to Au atom substituting the Ni atoms of substrate (Black line)
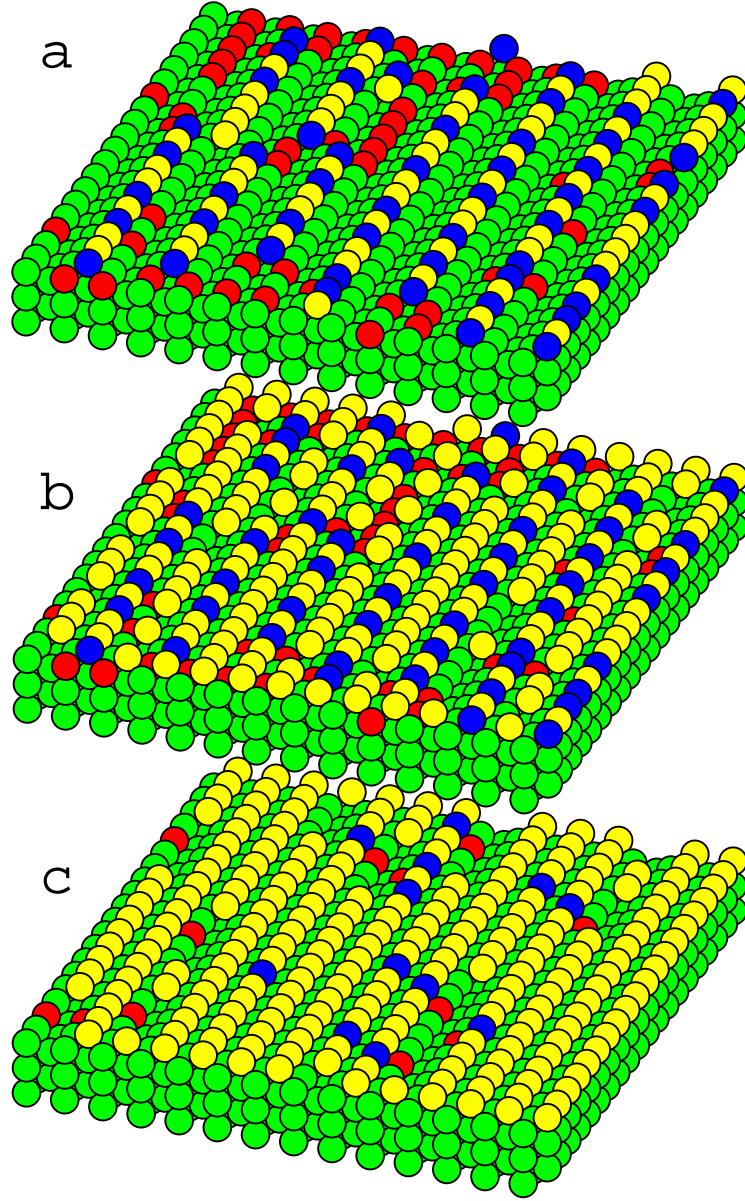
Figure 4: The de-alloying of Au/Ni(110)(Temperature 300K). (a) Surface structure at 0.40ML Au Coverage; (b) 0.8ML Au Coverage form through Configuration of Figure(a) deposited another 0.40ML Au atoms; (c) Monte Carlo Relaxed Surface structure from (b).
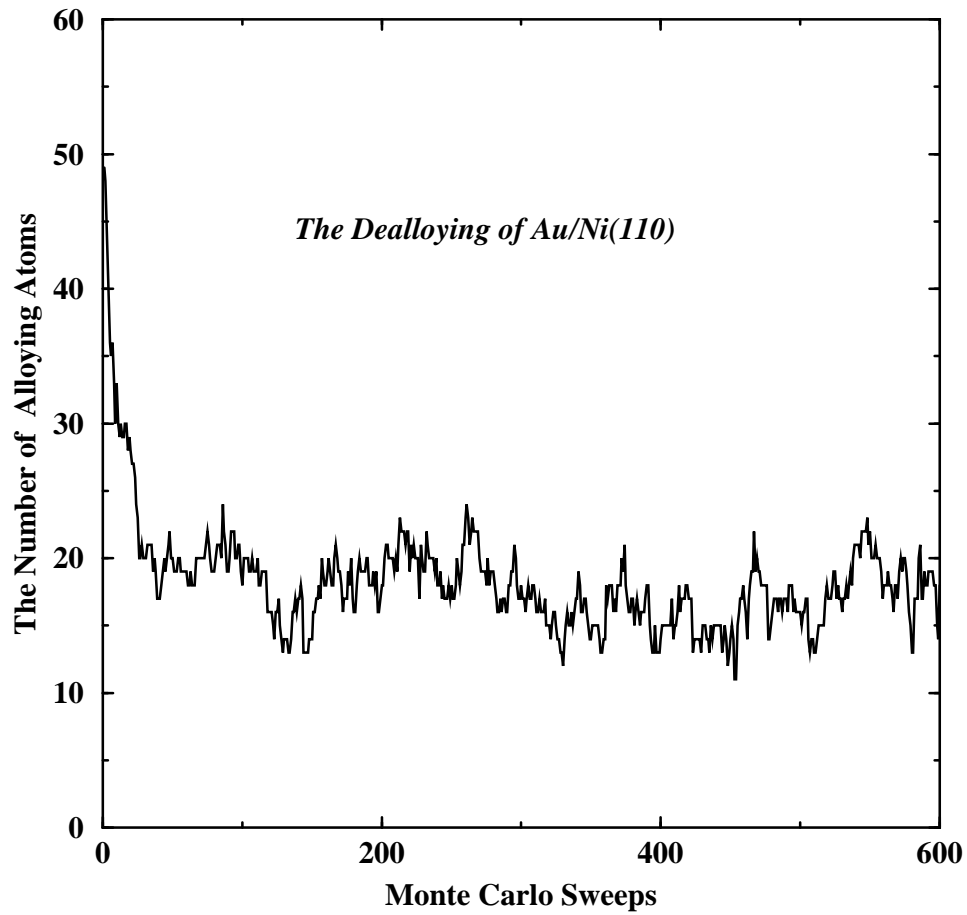
Figure 5: The change of the number Au atom with Monte Carlo Steps in the event form Fig.4(b) to Fig.4(c)
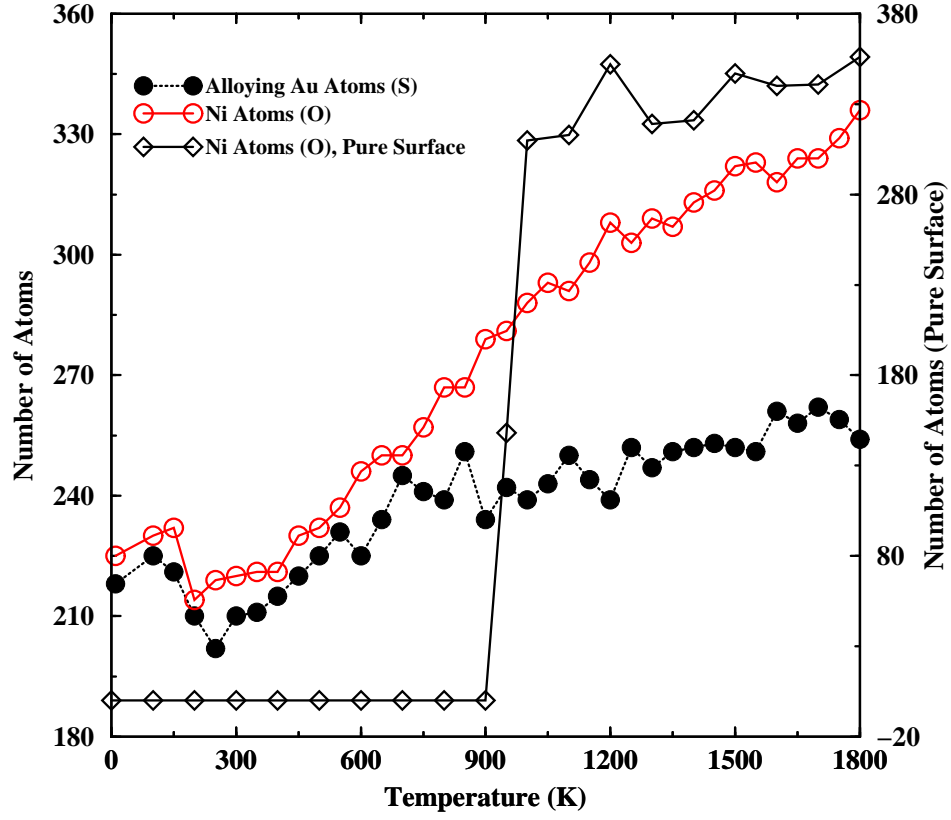
Figure 6: The changes of the numbers of the Ni atoms alloying and on surface with increasing temperature. (Red Circle) Ni atoms on surface; (Black filed Circle) Alloying Au atom; (Black Diamond) Ni atom on surface in system of pure Ni(110) sufcace