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Energy of the surface segregation of Ag atoms in Ag–Au alloys in an aqueous solution

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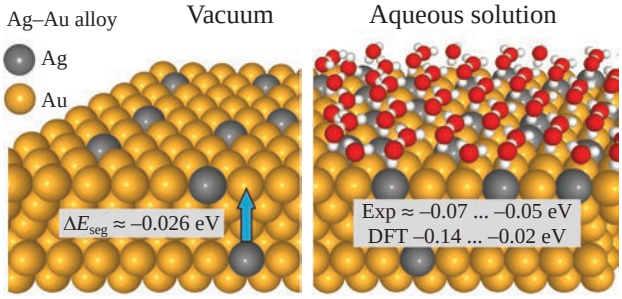
Segregation energy of Ag atoms in Ag(3%) and Ag(10%) silver–gold alloys is more than two times decreased upon the transition from vacuum to aqueous solutions. The DFT calculations using the (111) face of Au as an example have revealed that the effect of $^{\cdot}OH$ radical adsorbed together with H_2O molecules on the surface Ag atoms on the segregation energy is comparable to that of a water monolayer. Both experimental and model dependences of the segregation energy and the coverage with Ag on the cluster charge and electrode potential were analyzed.



Keywords: silver–gold alloy, surface segregation, surface enrichment, DFT, water adsorption.

A considerable step in understanding of the surface segregation was a switch from studying the alloy/vacuum interface[1–6] to investigations of alloy/water interfaces.[7] This step is of great practical importance since the majority of chemical and electrochemical processes proceed in aqueous solutions on surfaces of the alloy-based catalysts.[8–12] The flowing process of surface segregation leads to a changes in the surface composition of alloy and thereby inevitably affects the catalytic activity.[13,14]

The adsorption energy of various contaminating impurities on the gold surface is low, so further investigations have been focused on Ag–Au alloys. An essential difference in the surface segregation of Ag–Au alloy *in vacuo* and aqueous medium is determined by an abnormally high value of the diffusion coefficient of silver. This phenomenon can be explained by a significant surface deformation during the mechanical renewal, so the process of Ag diffusion occurs inside a sufficiently thin (~3 nm)[7] surface layer, proceeding due to a decreased surface tension of the alloy upon its contact with an aqueous electrolyte.[15] Due to these factors, the coverage of surface with silver can be carried out in an aqueous solution at room temperature.

In contrast to the previous experimental[17] and theoretical[16–19] studies of this system, the present work was aimed at the determination of segregation energy for silver atoms in Ag–Au alloy being in contact with an aqueous electrolyte.

Surface coverage of Ag–Au alloys with Ag (3 and 10%) was measured using laser temperature jump (LTJ) and cyclic voltammetry (CV) methods according to the known procedures.[7,20] Once the surface was conditioned, the electrodes were potentiostated in a 0.1 M NaF solution acidified with H_2SO_4 to pH ~5 during *ca.* 12 h under applied open-circuit voltage of 0.15 V relative to a saturated calomel electrode (SCE). In contrast to the reported data,[6] the NaF solution was cleaned from organic impurities using UV radiation in order to minimize any effects of the surface contamination. The surface coverage with Ag was defined as an average value for ten individual measurements. According to the LTJ and CV data, this surface coverage was 30 ± 10 and 50 ± 10% for the Ag(3%) and Ag(10%) electrodes, respectively. A duration of the electrode potentiostating prolonged up to 24 h did not result in any significant increase of coverage with Ag, which allowed us to consider these conditions as close enough to the equilibrium. Hence, the surface coverage with Ag in an aqueous environment, *e.g.*, for the Ag(10%) electrode, was twice higher than that in the case of vacuum.[1–4]

According to the McLean model,[21,22] the surface coverage with a segregating component may be described as:

$$\theta/(1-\theta) = \chi/(1-\chi) \exp(-\Delta G_{seg}/k_B T), \quad (1)$$

where θ and χ are the surface coverage with the active component and its molar fraction in the bulk alloy; k_B is the Boltzmann's constant; $\Delta G_{seg} = \Delta E_{seg} - T\Delta S_{seg}$ is the free energy of segregation, which is a difference between the free energy of atom in bulk and on the surface; ΔE_{seg} and ΔS_{seg} are the energy and entropy of segregation, respectively. The value of $\Delta G_{seg} < 0$ corresponds to a thermodynamically spontaneous process. To simplify the model, any entropy contribution can be neglected since ΔS_{seg} is less than k_B according to the previous estimations,[23] and consequently, the expression $\Delta G_{seg} \approx \Delta E_{seg}$ can be considered.

Approximation of the data[1–4] reported previously for the polycrystalline surface *in vacuo* (Figure 1, curves *1*–*4*) by the expression (1) has resulted in the value of $\Delta E_{seg} \approx -0.026$ eV, while the data[5,6] known for the (111) and (100) faces were close enough to those for the polycrystalline surface (see Figure 1, curves *5* and *6*). Faces of the alloy (see Figure 1, curves *5*–*7*) containing a small molar fraction of silver ($\chi < 0.15$) have demonstrated a noticeable tendency to reduce the segregation energy that coincides with the increase in the surface tension in the following order: $\gamma_{111} < \gamma_{100} < \gamma_{110}$. Analysis of the data for an aqueous solution has revealed the value of the segregation energy

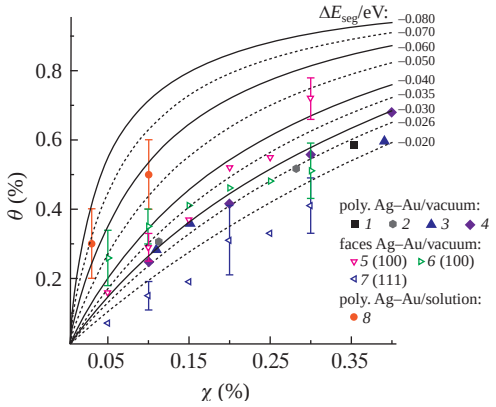


Figure 1 Relationship between the bulk χ and surface θ fraction of Ag: curves *1*, *2*, *3*, *4* represent the polycrystalline surface *in vacuo*; *5*, *6*, and *7* are given for the (100), (110) and (111) faces *in vacuo*, respectively; and *8* is plotted for the Ag(3%) and Ag(10%) electrodes in an aqueous solution. These lines depict the series of functions upon the calculated variation in ΔE_{seg}. Curves *1–4* herein were plotted using the data from refs. 1–4, respectively, while curves *5–7* are based on the data from refs. 5 and 6.

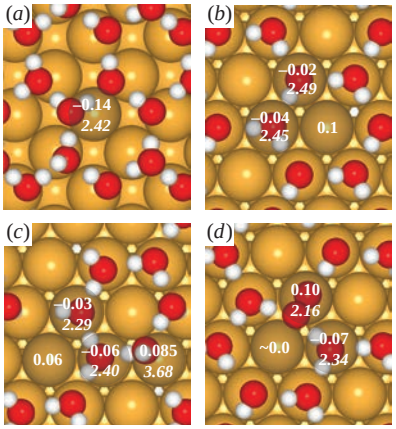


Figure 2 Energies of the segregation of one Ag atom (in eV) at various positions at the clusters surrounded by H_2O, $^{\cdot}OH$, and O_2 molecules. The values are given for: (*a*) the (100) Au face and H_2O monolayer, (*b*) the (111) Au face and H_2O monolayer, (*c*) the (111) Au face, H_2O monolayer, and $^{\cdot}OH$, (*d*) the (111) Au face, H_2O monolayer, and O_2. The distance between the oxygen and metal atoms is shown in italics and expressed in Å.

(ΔE_{seg}) ranging from –0.07 to –0.05 eV [see Figure 1, curve *8*]. Therefore, the main parameter being changed upon the transfer from vacuum to a solution is the observed double decrease in the segregation energy.

The application of equation (1) to analyze the experimental data[7] acquired previously for the mechanically recovered Ag(3%) electrode has revealed that the energy of surface segregation decreases from –0.07 to –0.14 eV (while θ varies from 0.35 to 0.9) upon the variation of E potential from –0.7 to 0 V. According to the data reported for water adsorbed at various metal systems such as Pd/Au(111)[24] or Ag(111),[25] a positive charge of the surface leads both to a sharp increase in the adsorption energy and to a decreased distance between the oxygen of water and the surface of metal cluster. A significant decrease in the adsorption energy upon potentiostating at the anode region[7] can consequently be explained by the decrease in the water adsorption energy and by the reorientation of water dipoles towards the metal surface possessing the potential being more positive than that of zero charge (*e.g.*, E_{PZC} ~0.03 V[26] for polycrystalline Au in NaF solutions).

To verify the assumption about the impact of water and its possible electrochemical splitting products[27] (oxygen, hydroxyl) on the segregation, a series of DFT calculations was performed using Quantum ESPRESSO[28] software package within the framework of generalized gradient approximation by the PBE[29] functional according to the Vanderbilt ultrasoft pseudopotential.[30] The (100) and (111) faces of Au were represented by its clusters consisting of 40 and 45 atoms, which is equivalent to five atomic layers. The initial geometry of water monolayer and other adsorbents was taken from other works.[31–33] The convergence criterion used in calculations was assumed as 10^{-4} eV, while the maximum force acting on the atoms was 10^{-3} eV Å^{-1}. The calculated values of $\Delta E_{seg} = E_s - E_b$ correspond to the difference between the energy of cluster bearing Ag on its surface (E_s) and the energy of cluster containing Ag in its center (E_b). Energies of Ag segregation *in vacuo* for the clusters represented by the (100) and (111) faces were 0.04 and 0.1 eV, respectively. The resulting discrepancy in the segregation values *in vacuo* for the (100) and (111) faces with the literature data ($\Delta E_{seg} \approx$ –0.026 eV) may be explained by two factors: the absence of any consideration of the small entropy contribution to ΔG_{seg} (see above why $\Delta G_{seg} \approx \Delta E_{seg}$) and the presence of several Ag atoms in nearest neighbourhood of the segregating atom.[†]

Aqueous monolayer has significantly changed the energy as compared to the case of vacuum, while the migration of Ag atoms towards the water molecules adsorbed at the cluster surface became thermodynamically advantageous (Figure 2). Obtained values for the segregation energy (ΔE_{seg} = –0.14 – –0.02) for the (100) and (111) faces covered with H_2O monolayer [see Figure 2(*a*,*b*)] are consistent with the experimental values of *ca.* –0.07 – –0.05 eV observed in an aqueous solution. A reconstruction of the (100) face of Au may proceed under aqueous electrochemical conditions that can lead to a decrease in the surface energy[34] and consequently to an increase in the negative value of ΔE_{seg} and to a decrease in the coverage of face surface. Adsorbed $^{\cdot}OH$ radical slightly increases negative values of the segregation energy up to –0.03 eV [see Figure 2(*c*)] as compared to the values of –0.06 eV for the H_2O monolayer at the (111) face of Au [see Figure 2(*b*)]. However, the O_2 molecules present on the surface dramatically affect the energies [see Figure 2(*d*)]. The H_2O molecules located at distances ⩾ 3.7 Å [see Figure 2(*c*)] cause an insignificant effect on the segregation. Therefore, the monolayer being in contact with the surface (< 2.5 Å) directly affects the segregation due to the metal–oxygen adsorption bonds formed, which compensates the deficient Ag–Au bonds of segregated Ag atom at the surface (coordination number of the segregated atom from bulk to the (111) face decreases from 12 to 9).

Since the metal–water and/or metal–hydroxyl bonds play a significant role in segregation, the energies of adsorption of H_2O molecule and $^{\cdot}OH$ on the metal surface were calculated (Table 1). These data allowed us to calculate ratios of the adsorption energies for H_2O molecule adsorbed on the metal and that on the golden cluster bearing the Ag atom on its surface, which were $E_{ads}(Au)/E_{ads}(Ag)$ = 1.04 and $E_{ads}(Ag_{seg}–Au)/E_{ads}$(Ag or Au) = = 1.46–1.52. In the case of $^{\cdot}OH$ radical, these ratios were $E_{ads}(Ag)/E_{ads}(Au)$ = 1.32 and $E_{ads}(Ag_{seg}–Au)/E_{ads}$(Ag or Au) = = 0.87–1.15, which has certainly confirmed that the higher binding energy for a surface atom with H_2O molecule contributes mostly to the Ag segregation. For $^{\cdot}OH$, the compensation of Ag exposure at the surface was a bit lower. The energy of H_2O adsorption on Ag atom located at the surface, which is higher than that in the

Table 1 The adsorption energies of H_2O molecule and $^{\cdot}OH$ radical on the (111) faces of Au, Ag, and the Au cluster bearing the Ag atom at the surface layer (Ag_{seg}–Au).

Cluster	$E_{ads}(H_2O)$/eV	$E_{ads}(^{\cdot}OH)$/eV
Au	–0.23	–0.41
Ag	–0.24	–0.54
Ag_{seg}–Au	–0.35	–0.47

[†] See Online Supplementary Materials for details.

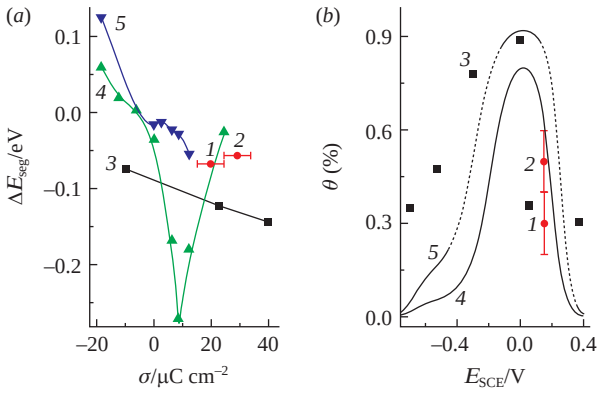


Figure 3 Estimated (*a*) energy of Ag segregation as the function of surface charge and (*b*) surface coverage with Ag as the function of electrode potential. Lines *1* and *2* correspond to the considered Ag(3%) and Ag(10%) electrodes, respectively. Line *3* also corresponds to the Ag(3%) electrode, but based on the data from ref. 7; curves *4* and *5* (*a*) are plotted using the data calculated for the (111) faces of Au at their positions equivalent to those shown in Figure 2(*b*) at –0.04 and –0.02 eV, respectively; and curves *4* and *5* (*b*) show the coverage calculated for the Ag(3%) and Ag(10%) Ag–Au alloys according to the model from ref. 35 and using data from ref. 15 for the surface energy of Ag and Au.

case of pure either Au or Ag clusters, can be attributed to the fact that the Ag atom belonging to the surface layer is surrounded by Au atoms, which results in a local positive charge at the Ag atom. This is in a good agreement with published data.[19]

To understand the reasons for changes in the coverage of Ag–Au alloy with Ag due to the potential, the values of ΔE_{seg} and θ were calculated as functions of the charge density and electrode potential (Figure 3) according to various approximations.[†] The ΔE_{seg} and surface coverage calculated by DFT according to the model[35] were consistent with the experimental data for the Ag–Au electrodes in aqueous solutions. The DFT-based calculations have revealed that the segregation energy significantly decreases upon growing the coverage of cluster surface [see Figure 3(*a*), curves *4* and *5*] and upon further increasing σ, this energy starts to rise again. This local decrease has to raise the coverage to its maximum value at certain potentials. The coverages [see Figure 3(*b*), curves *4* and *5*] calculated on the data reported previously for the surface energy[15] of (111) faces of Au are also in good agreement with the experimental data [see Figure 3(*b*), curves *1* and *2*]. The θ *vs.* E dependencies calculated herein for the surface coverage exhibit a local growth at ~0 V, so the offset potential of 0 V to cathode or anode regions has to significantly decrease the surface coverage with Ag.

Higher water adsorption at the surface Ag atom (as compared to that in the case of pure metals) makes the surface segregation thermodynamically advantageous. The contribution of ˙OH radical to the ΔE_{seg} value is comparable to that of the H_2O molecules. The most reasonable explanation for the ΔE_{seg} decrease in the Ag–Au system upon an anode shift is a change in the energy of adsorption of H_2O molecule at these metals. From model assessments based on the literature data for the surface energy, the maximum coverage with Ag was assumed as occuring at the potentials close to zero.

In conclusion, this work can be of interest for a scientific community staying far apart from the theoretical description of Ag–Au alloys as a model system, because the approaches reported herein may be applied to search for the tailored compositions and operating potentials to achieve the best electrocatalytic efficiency for considered alloys.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.008.

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