Gas adsorbate-induced Au atomic segregation and clustering from Cu(Au)

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ABSTRACT Surface compositional and phase segregation in an alloy can change its functionality, especially for applications where surface structure and chemistry play a vital role. For instance, the surface status of alloy catalysts significantly affects their catalytic performance for both heterogeneous and electrochemical processes. Surface segregation is believed to be driven by the difference in surface energy to reduce the total free energy of the alloy. However, the atomistic processes during the segregation process remain elusive, especially for gas molecule-induced segregation, where both structural and chemical reordering may occur. Herein, we achieved *in-situ* atomic-scale visualization of the surface segregation behaviors of a solid solution Cu(Au) alloy under the CO gas by an aberration-corrected environmental transmission electron microscope. CO-induced Cu(Au) surface ordering structures largely change the surface chemistry of the alloy. Further gas exposure at elevated temperature could facilitate Au atom diffusion through a specific “atomic channel” structure for dealloying and clustering on the surface. The segregated Au nanoparticles show rich phase and morphological dynamics interacting with the alloy surface, where the gas adsorption also plays an important role. These atomic insights provide direct evidence for the surface segregation and dealloying mechanisms of bimetallic alloys, and highlight the role of gas adsorbate in these surface processes.

Keywords: surface segregation, clustering, Cu(Au) alloy, environmental TEM, CO

INTRODUCTION

The alloy has long been found to go through surface segregation, that is, one constituent is enriched near the surface, which may be accompanied by the surface phase change. The major thermodynamic driving force is the difference in surface energies of alloy constituents—the element with lower surface energy tends to relocate to the

alloy surface. Besides, strain in the alloy caused by the difference in atomic radii of alloy constituents could also lead to surface segregation that relaxes the strain level of the alloy system. The above surface segregation behaviors related with “chemical bonding” and “strain” theories have been extensively studied [1–5]. The third type of surface segregation, that is, surface adsorption or surface reaction of gas molecules with one component of the alloy may cause a significant enrichment of that component in the surface of the alloy, receives much less attention [6]. Nevertheless, this type of surface segregation is of great interest for gas-phase heterogeneous catalysis [7] because the metallic surface of catalysts in “working condition” may differ from their “stationary status”, both structurally and chemically. And, the dynamic nature of the catalyst’s surface plays a decisive role in transforming gas reactants to products. The surface phase and ordering status of bimetallic catalysts are known to be responsible for their superior catalytic properties for a number of catalytic reactions which are more active than their pure counterparts [8–13]. On the other hand, tuning the surface plane, atomic structures, phase, strain and composition of alloy catalysts have created an arsenal of surface engineering strategies to optimize catalytic properties, which are all significantly affected by surface segregation behaviors of alloys.

Surface segregation is often limited to the surface and subsurface atomic layers, hence it is usually investigated under ultra-high vacuum (UHV) conditions with surface-sensitive techniques such as Auger electron spectroscopy (AES), low energy ion scattering spectroscopy (LEIS) and low energy electron diffraction (LEED) [14,15]. However, these techniques often lack direct imaging methods with site-specific information and are incompatible with a required reactive gas environment. Scanning tunneling microscopy (STM) has been a major tool to image the

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surface structure directly, but the information is often limited to the surface and subsurface. Also, the structural dynamics under continuous gas supply is not convenient to obtain due to the mode of “scanning” imaging. Meanwhile, surface segregation may lead to structural and chemical changes beyond subsurface, i.e., a few nanometers deep into the bulk or nanomaterials. Hence, *in-situ* atomic-scale observations of the whole surface-to-bulk region under the dynamic segregation process are essential to decipher underlying atomistic processes and mechanisms. Aberration-corrected environmental transmission electron microscope (AC-ETEM) has emerged as a powerful tool to characterize the dynamic atomic structural change under a gas environment for catalysis research [16–22]. The order-disorder transition on Cu(Au) surface has been found, and the inter-diffusion of constituent atoms can lead to the formation of dislocations near the alloy surface [23,24]. Herein, we demonstrate that surface segregation of Cu(Au) solid solution alloy could lead to various surface ordering structures and the nucleation of Au nanoparticles on the surface under the CO exposure. Dynamic structural evolution during the surface segregation and dealloying process has also been captured, which highlights the rich dynamics of surface segregation behaviors under gas exposure.

EXPERIMENTAL SECTION

Materials preparation

A model Cu-Au solid solution alloy (Cu and Au atoms are randomly mixed) thin film (~50 nm thick) with an Au atomic concentration of ~10% was prepared by a UHV e-beam evaporation system. The as-prepared Cu-Au thin film is single crystal (100) with a thickness of ~50 nm.

AC-ETEM experiments

The Cu-10 at% Au thin film was removed from the substrate and mounted on TEM grids through floating in deionized water. A double-tilt Gatan®628 holder was used for heating in a ThermoFisher®Titan ETEM with an objective-lens corrector operated at 300 kV, which has a base pressure of $\sim 10^{-8}$ mbar. CO gas was introduced into the ETEM column with a pressure of 0.001 mbar through a leak-valve controlled by ETEM vacuum system. The gas composition was confirmed *via* a residual gas analyzer (RGA) with sensitivity down to 10^{-11} mbar (near the sample area). All experiments were performed at 350°C.

HRTEM image simulation

The high-resolution TEM (HRTEM) image simulation of

the Au NP was carried using the multislicing method, which is integrated into the code “SimulaTEM”, as is described in the published paper [25]. The parameters for the image simulation were chosen as follows: accelerating voltage of 300 kV and a spherical aberration coefficient of the objective lens of 2 μm .

RESULTS AND DISCUSSION

We used a model single-crystalline Cu(Au) solid solution alloy (Cu and Au atoms are randomly mixed) thin film (~50 nm thick) with an Au atomic concentration of ~10% prepared by a UHV e-beam evaporation system. The as-prepared Cu-Au thin film was mounted on a heating holder for use in the AC-ETEM. A heating temperature of ~350°C and a CO partial pressure of $\sim 10^{-3}$ mbar were used in all *in situ* gas-heating experiments. Real-time HRTEM imaging was made from a cross-sectional view of different surface planes, enabling a clear view of both surface and subsurface atoms.

Surface segregation-induced atomic ordering

The schematics in Fig. 1a illustrate the general behaviors of surface segregation, dealloying and clustering process of the Cu-Au alloy. Fig. 1b and c present typical HRTEM images of pristine Cu-Au (010) and (110) surfaces with no observable surface ordering in a vacuum ($< 1 \times 10^{-8}$ mbar) at 350°C. Upon CO exposure, surface re-ordering happens on all surfaces after a staging period (~30 min), i.e., Au atoms diffuse to the surface and form a series of ordered structures on the alloy surface. Fig. 1d–i illustrate these surface ordering structures for (010), (110) and (120) surface planes, respectively. In Fig. 1d, the HRTEM image shows a periodicity of brighter and weaker spots in both surface and subsurface atomic layers of (010) surface.

The enlarged image in Fig. 1e shows a good match between the experimental HRTEM image with the corresponding simulated image based on the atomic model of the CuAu-I phase (Fig. S1). Similarly, Fig. 1f–i demonstrate the surface ordering structures, both with a structural motif of CuAu₃ phase (Fig. S1) that is enriched with Au atoms on (110) and (120) surfaces. It is noted that a higher indexed (120) surface can be reconstructed to a double-stepped surface as shown in Fig. 1h, i, and this surface structure can be easily extended to other high-indexed Cu(Au) surfaces. In addition, lattice distance of {100} plane and fast Fourier transform (FFT) image of Fig. 1h are also shown in Fig. S2, which can match well with ordered CuAu₃ phase. These results collectively reveal that the disorder-to-order transition is

Figure 1 Atomic-scale surface segregation of Cu-Au alloy. (a) Schematics of the Au surface segregation and clustering process on the Cu(Au) alloy upon CO exposure. (b, c) Typical HRTEM images of pristine Cu(Au) (010) and (110) surfaces with no observable surface segregation in a vacuum. (d–i) HRTEM images of the surface ordering structures for (010), (110) and (120) surface planes and enlarged images are presenting good matches with simulated images based on atomic models of different ordering phases. Scale bars are 1 nm (b, c, d, f, h), and 5 Å (e, g, i), respectively.

a general behavior for a solid-solution binary alloy, and the Au concentration can be readily enriched to 75 at% of CuAu_3 ordered phase on the Cu-Au surface.

The above Au atom segregation-induced ordering at the Cu(Au) surface can usually reach a thermodynamic equilibrium when the total surface energy and strain energy are minimized by these ordering structures. Surprisingly, in the presence of CO, we observed further surface segregation-induced dynamic structural changes near the surface with elongated exposure time. After

60 min of staging under CO gas at 350°C, some stepped alloy surfaces went through more complicated compositional segregation accompanied by vigorous atomic rearrangement. In Fig. 2a, multiple atomic steps are present on the Cu(Au) surface, which consists of (010) surfaces and some higher-indexed sloped surfaces connecting them (white arrows). These surface steps do not adopt surface reconstructed structures observed in Fig. 1, but show unique atomic structures (bottom-left insets) featuring a gradual increase of the lattice distance between

Figure 2 “Atomic channeling” facilitates surface segregation in CO. (a) HRTEM image shows multiple surface steps with different stages (I to IV, white-dashed line boxes) of Au surface segregation process defined by the lattice distance between surface and subsurface layer (insets). (b) The typical HRTEM image presents the atom rearrangement near surface step during the segregation process, which may enable a possible “atomic channeling” path for diffusion. (c) Intensity profile shows the disorder-to-order transition of Cu(Au) lattice along the direction from bulk to surface (yellow arrow in (b)). (d) Detailed structural analysis of the “atomic channeling” shows an increase of lattice distance from 3.66 to 5.10 Å for the upper terrace and a decrease of lattice distance from 3.96 to 2.11 Å for the upper terrace. The scale bars are 1 nm (a), and 5 Å (b, d), respectively.

the surface and subsurface. Depending on the degree of lattice expansion, stages I, II, III, and IV are labeled for different surface steps, although they are captured at the same time. The up-right insets clearly illustrate this gradual change of the step-edge areas, where the lattice distance between the surface and subsurface atom layers keeps increasing from 1.98 to 3.31 Å (white double-arrows) while the lattice distance between the subsurface layer and the 3rd sublayer keeps decreasing from 1.98 to 1.75 Å (black double-arrows). This trend of lattice expansion between the surface and subsurface planes has also been found on (100) surface plane (labeled by yellow indexes), which means it is isotropic for the cubic structure. As shown in the later stage (IV) of this surface

change, one or more atom columns are missing between the surface and subsurface layer as indicated by the white-dashed ellipse.

As shown in Fig. 2b and Movie S1, a (010) terrace with a half adlayer (white arrow) becomes the dominating structure on these stepped alloy surfaces. This “terrace-adlayer” structure features a (010) terrace separated by two (110) slope surfaces, and a half adlayer is covered on the (010) terrace extending from upper (110) surface. One subsurface (010) atomic plane (white arrow) beneath the half adlayer extends from the bulk alloy to the surface and merges with the (010) adlayer. This structural relaxation leads to a disorder-to-order transition in the atomic plane beneath the adlayer (yellow arrow). The intensity profile

of atoms in this plane from bulk to the surface is drawn in Fig. 2c, which shows a clear disorder-to-order transition along this atomic plane. This is also accompanied by the increase of Au concentration from the bulk to the surface but with a deeper penetration to the bulk comparing those surface ordering structures in Fig. 1. In addition, atomic layer shown by the white arrow in Fig. 2b disappears gradually between the surface and subsurface atom layers in (010) adlayer (Fig. S3), while the intermediate region between them is still occupied by some atomic columns. This observation explains the large expansion from 1.98 to 3.31 Å (stages I to IV).

Detailed analysis in this region reveals a possible Au diffusion channel from bulk to the surface enabled by this “terrace-adlayer” structural feature. As shown in Fig. 2d, two big white arrows indicate the atomic layers above and under the disorder-to-order transition layer, which go through a large expansion from bulk to the surface. The $d_{(010)}$ increases from 3.66 Å (Cu-10 at% Au) to 5.10 Å near the step-edge and this expanded lattice should largely promote Au diffusion from bulk to the surface. Two white-dashed boxes show a structural unit with its structure and dimension identical with that of Au_3Cu (~3.96 Å). These two units are right on the connection between the (110) slope and the (010) adlayer, which initiates a surface structure transition from a lattice distance of two (020) layers (~3.96 Å) to around one (020) layer (~2.11 Å) as shown by two black arrows. This two-to-one atom layer transition leads to the diminishing of atoms, and thus frees the space above the “disorder-to-order” layer. These observations illustrate complicated segregation-induced atomic restructuring and also chemical modifications at the surface and near-surface regions, especially at the stepped alloy surface. These changes are primarily induced by the tendency of Au segregation driven by strong CO-metal interaction, especially for those low-coordinated atoms near step edges. Au and Cu atoms have been reported to have a good affinity to CO molecules and form Au-CO or Cu-CO species under CO gas at elevated temperature [26–28]. These behaviors are absent under thermal-only conditions, which highlights the effect of gas adsorbate on surface segregation. It is also noted that the surface diffusion also promotes this segregation behavior kinetically, where the enhanced surface diffusion caused by large surface area and the presence of surface steps can facilitate the exchange of Au and Cu atoms on the alloy surface.

Nucleation of segregated Au atoms

Dealloying and clustering at the surface often require

large chemical driving force beyond the traditional regime of surface segregation. Here, we find elongated CO exposure could induce such a phenomenon, that is, Au segregation leads to the nucleation of Au nanoclusters on the alloy surface, as shown below. In Fig. 3, two different modes of Au nucleation have been observed. The first one proceeds through gradual segregation of ordered Au clusters at step-edge sites with an epitaxial interface. Time-resolved HRTEM images recorded this process in Fig. 3a. Initiated at step-edges indicated by two white arrows, Au atom clusters increase their dimensions laterally with time and eventually reside on the terraces created by the segregated atoms. Au atoms pre-segregated to the high-indexed alloy surface (Fig. 1d–i) can be the source of Au atoms to form this type of Au clusters through short-length diffusion. The surface steps are covered with Au clusters, which lowers the total free energy in this model. Hence, these Au clusters are stabilized on these steps rather than merge into bigger nanoparticles. The second mode also initiates from the step-edge but the nucleus does not follow the epitaxial relationship with the substrate, as shown in time-resolved HRTEM images in Fig. 3b and Movie S2. The Au atoms aggregate on the step-edge and evolve from a disordered structure to a nanoparticle as shown in Fig. 3c, which possesses a well-defined face-center-cubic (FCC) structure with well-faceted (111) and (010) planes (Fig. S4). It is noted that these two modes can trace back to the specific “terrace-adlayer” structure (indicated by white dashed-line boxes described in Fig. 2), which disappears after the surface clustering as seen in the image of 76 s in Fig. 3a and the image of 58 s in Fig. 3b. This observation indicates the dealloying and clustering of Au atoms are largely facilitated through the unique “atomic channeling” process.

Through surface segregation and clustering, Au atoms either form supported nanoparticles (Fig. 3d) or coherent interface (Fig. 3f) with alloy substrate with an epitaxial relationship. As shown in Fig. 3d, a gold nanoparticle with a size of ~4 nm is supported on the (110) surface and corresponding FFT pattern shows a good epitaxial relationship between them. It is noted that considerable strain exists in the particle-substrate interface as shown in the strain analysis from the HRTEM image in Fig. 3e. As shown in Fig. 3f, a coherent interface is shown in the HRTEM image and the corresponding FFT pattern, but one transition region (TR) with “band-like” structure can be observed between Au and the alloy substrate. Detailed analysis shows no misfit dislocation was formed at the interface between the CuAu substrate and TR while sev-

Figure 3 *In situ* observation of Au segregation and clustering. (a, b) Time-resolved HRTEM images show two different nucleation modes (epitaxy vs. particle) of Au clustering at step-edges. (c) Typical HRTEM image of a segregated Au nanoparticle stabilized at the step-edge of Cu-Au substrate. (d) HRTEM image and corresponding FFT pattern show an epitaxial relationship between the segregated Au nanoparticle and alloy substrate. (e) The corresponding strain analysis shows a strained interfacial area (white-dashed line ellipse in (d)). (f) HRTEM image and corresponding FFT pattern show segregated Au atoms “wet” on the surface, and a TR forms between an intimate epitaxial interface and the alloy substrate. (g) Strain analysis of the “inter-band” atomic structure shown by rectangular zone in (f). All the scale bars are 1 nm.

eral misfit dislocations were formed at the Au/TR interface as shown by the strain analysis in Fig. 3g and Fig. S5. Since the lattice of “band-like” TR is acquired under different defocus values (Fig. S5), we deduce that “band-like” structure in TR was formed by atomic-scale bending. Diffusion of Au atoms from alloy to the surface results in an Au concentration increase in TR while maintaining a coherent interface between them. Atomic-scale bending can be seen as a superstructure that releases the lattice mismatch between alloy substrate and TR.

Stability of Au clusters on alloy substrate

After Au atoms have segregated to the alloy surface in the form of supported nanoclusters, they show rich dynamic interaction behaviors with the substrate. We find surface steps play a critical role in stabilizing these supported Au

clusters. Time-resolved HRTEM images in Fig. 4a captured from Movies S3 and S4 present how an Au nanocluster near a step-edge changes its crystallographic orientation with substrate not only by rotating but also by reshaping its morphology to transform between two metastable states. It should be noted that we can clearly see the lattice of Au cluster only if the speed of morphological change is slower than the temporal resolution of the camera (~ 0.5 s), and the observed phase can be considered as a metastable state. In the image of 0 s, the Au cluster is located on a step with 2 layers of (020) lattice, and the interface between Au cluster and substrate has a semi-coherent relation that the Au (111) plane is extended from (020) plane of the alloy with a small tilt as indicated by the yellow dashed line. Obviously, this interface is in a metastable status because of the large dif-

Figure 4 Dynamic balance of segregated Au nanoparticles induced by CO adsorption. (a) Time-resolved HRTEM images show the rotation and morphological change of an Au nanoparticle near a step-edge. (b–e) HRTEM images and the corresponding FFT patterns demonstrating various Au cluster-substrate orientations during the dynamic movement of cluster Au. (f, g) HRTEM image and the schematic of the Au nanoparticle with equilibrium shape using the Wulff construction, respectively. (h) Enlarged image of the rectangular zone in (f) shows possible “single” Au atom on the surface. The scale bar in (h) is 2 Å, all other scale bars are 1 nm.

ference between the lattice distance of Au (111) ~ 2.35 Å and CuAu₃ (020) ~ 2.0 Å. Hence, it quickly changes its shape through atomic rearrangement in the nanocluster and reaches a stable status after 13 s. The final cluster-substrate orientation is close to a cube-on-cube epitaxial but with a small tilt (indicated by two yellow dashed lines), and three lattice-mismatch dislocations are found on their interface.

We captured various cluster-substrate geometries during the dynamic movement of Au cluster on the substrate as shown in Fig. 4b–e and Fig. S6. Two metrics can be seen from the corresponding FFT patterns below the

HRTEM images, i.e., the number of atomic layers of the step and the cluster-substrate orientation. In Fig. 4b, c, the Au clusters are both in a cube-on-cube epitaxial relationship with the substrate, i.e., (001)[100]_{Au}//(001)[100]_{Sub} with 1 layer and 2 layers of (020) atomic plane, respectively. In Fig. 4d, the Au cluster shows a small tilt ($\sim 4^\circ$) between its (220)_{Au} plane and (100) plane of the substrate with a three-layer step. In Fig. 4e, the cluster-substrate orientation is (1 $\bar{1}$ 1)[110]_{Au}//(001)[100]_{Sub}, and it also resides on a three-layer step site. According to the Wulff construction theory, the Au cluster can reach an equilibrium shape with all low-indexed {100} and

{111} surfaces exposed as seen in Fig. 4f, g and Fig. S7. Au particles can extend into the Cu(Au) substrate, as shown by the dotted arc in Fig. 4f and Fig. S8, where the interfacial strain is mediated by misfit dislocations. From the HRTEM image of an enlarged area (white box in Fig. 4f), we could also spot traces of separated Au clusters down to single atom as indicated by white arrows in Fig. 4h, which indicates a mass transport may be ongoing between the nanoparticle and alloy substrate.

The above observation of dynamic interaction of supported Au nanoparticles with substrate indicates that the particle-substrate orientation is not fixed and can be tuned by a small perturbation caused by local thermal and/or chemical fluctuation. Meanwhile, the Au nanoparticle can go through atom restructuring to response to this local variation and reach several metastable states. Therefore, we provide a semi-quantitative model to describe this gas-adsorbate involved structural dynamics of supported clusters. Morphology of Au nanoparticles and structural relation with the substrate are governed by the total free energy contributed by surface energy of the Au nanoparticle, particle-substrate interfacial energy and adsorption energy of CO gas molecules. We focus on two of the most stable states during the dynamical changes of

cluster-substrate relationship as shown in Fig. 5a, b, both of which last for a few seconds in our video recording. It is seen that the Au nanoparticle in Fig. 5a is close to the equilibrium shape, and two misfit dislocations can be observed, while one misfit dislocation exists in Fig. 5b. The interfacial area of Au nanoparticle and Cu(Au) substrate decreased gradually from Fig. 5a to b. This “dewetting” process is clearly shown in the Movie S3. Thus, we assume that the out-most Au atoms on {111} facets of Au nanoparticle are detached layer by layer in this “dewetting” process, as shown by Au atoms (tan color) and the black arrows in Fig. 5c.

In order to quantify the systematic energy, Fig. 5c–e show the schematic to calculate the change of surface energy of Au nanoparticle (details in the Supplementary information). We use a generalized Wulff-Kaisheff theorem [29] to roughly quantify the supported Au nanoparticle under CO gas environment as follows. The total free energy (E) is composed of the surface energy of Au nanoparticles (σ), Au/Cu-Au alloy interfacial energy (E_N) and the adsorption energy of CO molecules (E_a), shown in Equation (1). And we use the following Equations (2) and (3) to acquire the total energy change per 0.05 nm ($\Delta E'$) with the interfacial width.

$$E = \sigma + E_N + E_a = \sigma + (E_d + E_\varepsilon)S + E_a$$

$$= \sum_{i \neq AC} \gamma_i S_i + (\gamma_{AC} - \gamma_C) S_{AC} + \left(\frac{G_A G_C (f - \varepsilon) b}{\pi (G_A + G_C) (1 - \nu)} \left(\ln \frac{R}{b} + 1 \right) + \frac{2 G_A (1 + \nu)}{1 - \nu} h \varepsilon^2 \right) S_{AC} + \sum_{j \neq AC} \gamma'_j S'_j \quad (1)$$

$$\Delta E = E - E_0 = \Delta \sigma + \Delta E_N + \Delta E_a$$

$$= \left[\gamma_{100} (S_{100}^1 - S_{100}^0) + \gamma_{111} (S_{111}^1 - S_{111}^0) \right]_A - \gamma_{100} \Delta S_C + \left[\frac{G_A G_C (f - \varepsilon) b}{\pi (G_A + G_C) (1 - \nu)} \left(\ln \frac{R}{b} + 1 \right) + \frac{2 G_A (1 + \nu)}{1 - \nu} h \varepsilon^2 \right] \Delta S_C \quad (2)$$

$$\Delta E' = E_{x_0+0.05} - E_{x_0} = (E_{x_0+0.05} - E_0) - (E_{x_0} - E_0) = \Delta E_{x_0+0.05} - \Delta E_{x_0} \quad (3)$$

where σ , for a crystal having i facets of area S_i characterized by the surface energy $\gamma_i S_i$. γ_{AC} is the interfacial energy density and S_{AC} is the contact area. $f = (a_A - a_C)/a_C$ is the epitaxial misfit between Au (lattice parameter a_A) and Cu substrate (lattice parameter a_C), which was shared by dislocations and strains. That is, f can be divided into the elastic strain ε and δ , misfit accommodation by dislocations. It means that there are N interfacial dislocations at the interface to release the misfit, and $\delta = N|b|/L$, in which b is Burger's vector component of misfit dislocations. So interfacial width L can be expressed to be $Nd + x$ ($0 < x < d$. d is the separation of parallel misfit dislocations), and S_{AC} can be roughly expressed to be L^2 . R is the distance to the outmost boundary of the dislocation's strain field. If

$2d$ is less than the height of Au particle h , then $R \approx d$. G_A , G_C and ν are the shearing modulus and Poisson ratio of Au and Cu, respectively. In addition, we provided the calculation process for systematic energy in Section “Total energy calculation” of Supplementary information and Figs S9, S10.

As shown in Fig. 5f, we assume that the initial interfacial width L of Au particle and Cu(Au) substrate is about $3d$. Since the lattices between Au and Cu substrate tend to be ordered in middle of adjacent two misfit dislocations ($0 < x < d$), there is one minimal value for the strain energy E_N , meaning that $\Delta E'$ increases first, then decreases in the range of $0 < x < d$. Positions of misfit dislocation illustrated by “ $N = 1, 2, 3$ and 4” are the

Figure 5 Thermodynamic characterization of the “dewetting” Au nanoparticles. (a, b) Time-resolved HRTEM images showing the dewetting process of Au nanoparticle on the Cu(Au) substrate. Both scale bars are 1 nm. (c) Schematic of the Au nanoparticle with equilibrium shape. We assumed that out-most Au atoms on {111} surface of Au nanoparticle were escaped layer by layer, as shown by tan Au atoms and the black arrows. (d, e) Schematic model of “atom peeling” process describing facet change (d) and the interfacial area change (e) of Au nanoparticle and Cu(Au) substrate. (f) Change of total energy E per 0.05 nm with the interfacial width.

abrupt drop in systematic energy, because one misfit dislocation disappears. This causes the instability of supported nanoparticles due to the structural relaxation. Besides, compared with the change of systematic energy, disturb of temperature change and CO flow may be the major factor causing the morphology and orientation instability of Au nanoparticles, when the interfacial width L is less than the separation of misfit dislocation d . Above analysis shows the origin of the interfacial structure instability between small nanoparticle and the support, which are encountered in real gas environment at elevated temperature.

Coalescence of Au clusters can also happen on the alloy

surface featured by a move-and-merge mechanism. In Fig. 6a, time-resolved HRTEM images illustrate four Au clusters (2–3 nm) gradually move and coalesce together one by one and finally form a nanoparticle (5–6 nm) as tracked by yellow-dashed circles. The final nanoparticle has multigrain with clear grain boundary as shown in Fig. 6b (0 s), and the grain boundary can disappear during continuous annealing and gas exposure after 380 s. This similar coalescence behavior is also found in liquid with the help of capping agents, demonstrating how five-fold symmetry Au nanoparticle is formed [30]. Our observations on further coalescence events can lead to similar results as shown in Fig. 6c, d. It is also noted

Figure 6 Coalescence of Au nanoparticles on the substrate. (a) Time-resolved HRTEM images show the coalesce process of four Au nanoparticles into a stable large Au nanoparticle. (b) Time-resolved HRTEM images show the process of diminishing of grain boundaries of a coalesced Au nanoparticle. (c, d) HRTEM images show the similar coalescence process of larger Au nanoparticles. All the scale bars represent 1 nm.

that the movement of small Au clusters is largely limited on the alloy surface, i.e., they can only migrate on the surface, in contrast with free-movement in liquid media; however, they share similar mechanistic features as shown above.

CONCLUSIONS

We investigate atomic-scale Au segregation-induced dynamic behaviors on the surface of a solid solution Cu-10 at% Au alloy under CO gas exposure at 350°C by AC-ETEM. We directly visualize a series of real-time observations induced by Au segregation including surface ordering, dealloying and nucleation of Au clusters and dynamic evolution of Au clusters to nanoparticles as well as their stability on the alloy surface. Remarkably, we find a unique atom channeling effect on the alloy (010) surface, which facilitates the Au atomic transportation from bulk to the surface during segregation. We also find various types of particle-substrate orientation relationships and rationalize it with a quantitative model considering surface energy, interface energy and gas adsorption energy, to explain how they transform among different geometries. These results provide atomic insights to the fundamental understanding of surface segregation and dealloying and can be extended to applications involving such alloy system such as phase evolution of supported nanoparticle catalysts.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details, supporting data and movies are available in the online version of the paper.

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气体吸附诱导Cu(Au)合金中Au原子的偏聚和富集

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摘要 合金中的表面成分和相偏析会改变其功能, 尤其是在表面结构和化学起着至关重要作用的应用中. 例如, 合金催化剂的表面状态显著影响其在异相催化和电化学过程中的催化性能. 表面成分偏析被认为是由表面能的差异驱动, 以减少合金体系的总自由能. 然而, 目前合金中成分偏析的原子尺度进程还尚不清楚, 尤其是对于气体分子诱导的成分偏析, 在该过程中可能同时发生结构和化学重排. 本文通过像差校正环境TEM从原子尺度研究了固溶态Cu(Au)合金在CO气氛下的表面偏析行为. CO气氛能够诱导Cu(Au)合金表面形成有序结构, 在很大程度上改变合金的表面化学性质. 高温条件下, CO气氛会进一步促进Au原子通过特定的“原子通道”进行扩散, 在合金表面偏聚和富集. 富集形成的Au纳米颗粒与合金表面在形貌和结构方面发生了丰富的动力学交互作用. 这其中CO气体吸附也起着重要的作用. 这些原子尺度的研究结果为双金属合金的表面偏析和去合金化机理提供了直接证据, 并突出了气体吸附物在这些表面行为中的作用.