

Hydrogen-Adsorption Induced Surface Segregation and Chemical Ordering in Cu-Pt Alloys

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Surface segregation of an alloy results in the surface enrichment of one of the alloy components. This phenomenon has a direct effect on technology-related properties of alloys because the resultant minor compositional changes at the surface can lead to significant changes in material properties ranging from corrosion resistance, catalytic performance and mechanical behavior. In addition to the compositional changes, surface segregation may induce structure changes in the surface and subsurface regions. Probing the segregation induced structural evolution has been a major challenge, mainly because of the experimental difficulties in resolving both the structure and composition evolution. Meanwhile, the circumstances under which surface segregation occurs vary and the nature of the segregation depends on the specifics of the surrounding environment. In general, the element with a smaller surface energy segregates to the surface under idealized conditions (i.e., for a clean surface) whereas the alloy element forming stronger bonds with gas species becomes enriched at the surface in a reactive environment[1]. Our current understanding of surface segregation under reactive conditions is largely derived from “quench-and-look” studies, from which dynamic changes in the surface composition and structure are difficult to extract.

Environmental transmission electron microscopy (ETEM) offers a unique window to monitor the surface composition and structure evolution at the atomic scale under the reaction conditions. Here we use ETEM to monitor the surface segregation of a Cu-Pt alloy in the hydrogen gas atmosphere and demonstrate the H adsorption induced Pt surface segregation and chemical ordering. The Cu-Pt alloy is chosen for its practical importance in catalysis. Cu-5at.%Pt(100) thin films with a nominal thickness of 50 nm were grown on NaCl(100) using e-beam co-evaporation of Cu and Pt. The alloy films were transferred from the NaCl substrate by flotation in deionized water, washed, and mounted onto a TEM specimen holder. The native Cu oxide was removed inside the TEM by annealing the Cu-Pt films at 600°C and 1×10^{-2} Torr of H₂ gas flow, which resulted in tears and holes with faceted edges being formed in the thin film. These freshly created facets are atomically clean and permit for cross-sectional TEM observation of elemental segregation induced structural changes in the surface region.

Fig. 1(a) illustrates a high-resolution TEM (HRTEM) image of a typical (100) facet, seen edge-on along the [001] zone axis, of the Cu-5at.%Pt(100) film at 600°C and 10^{-2} Torr of H₂ flow. The (100) surface displays a seemingly unreconstructed (1×1) surface structure. However, a careful examination shows that the outermost surface layer has developed into a Cu-Pt ordered surface alloy that has a superlattice feature with alternate bright and faint contrast of atomic columns. This can be further discerned from the enlarged view of the surface region (the upper-right inset in Fig. 1(a)) and the intensity profile along the topmost layer (marked by the yellow line). In the Cu-Pt system, Cu has a smaller surface energy than pure Pt and is favored at the surface [2]. Because of the high dissociation barriers of H₂ molecules on Cu surfaces and non-bonding of atomic H with Cu at temperatures greater than ~80°C [3,4], the observed formation of the Cu-Pt ordered surface alloy is attributed to the preferential hydrogen

adsorption toward Pt atoms, which results in surface segregation of Pt and chemical ordering. To further elucidate the atomic structure of the surface alloy, density-functional theory (DFT) modeling is performed to examine H adsorption and the resulting Pt surface segregation. The bottom-left inset of Fig. 1(a) shows the DFT obtained structure of the Cu-Pt ordered surface alloy, in which H atoms are found to adsorb preferentially at the hollow sites and bind to Pt atoms. The DFT-obtained structure is used to perform HRTEM simulations for comparison to the experimental HRTEM images. The upper-left inset of Fig. 1(a) shows a simulated image and the intensity profile along the topmost layer, which reproduce the characteristic superlattice contrast and are broadly consistent with the experimental HRTEM image. Fig. 1(b) illustrates an HRTEM image of a (410) facet, showing the segregation of Pt atoms to step edges and their next nearest neighbors, as indicated by their stronger image intensity (upper-right inset). The bottom-left inset of Fig. 1(b) shows the DFT minimum-energy structure of the (410) surface, where H atoms are found to adsorb to the hollow sites (for terraces) and the bridge sites (for steps) and bind to Pt atoms. The simulated HRTEM image and the intensity profile along the surface terrace (upper-left inset in Fig. 1(b)) match well with experimental HRTEM image [5].

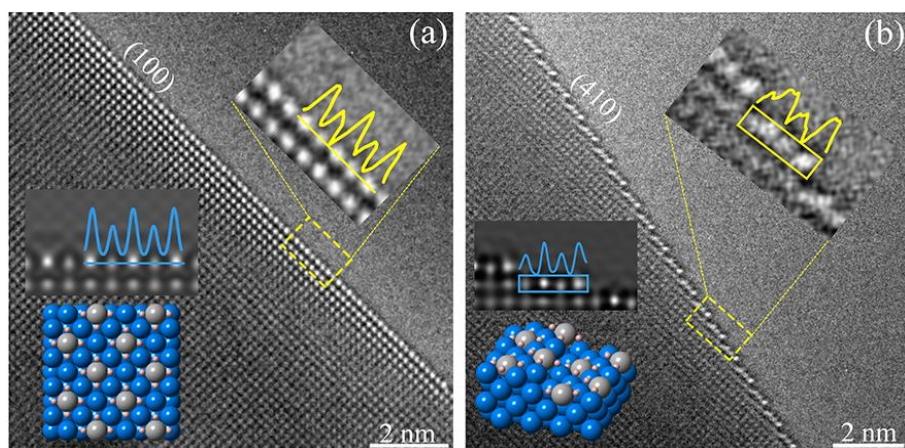


Figure 1. In situ HRTEM imaging of the Cu-5at.%Pt(100) at 600°C and 10⁻² Torr of H₂ flow. (a) HRTEM image of the (100) surface showing the formation of a Cu-Pt ordered surface alloy. Upper-right inset: enlarged view of the surface region and the intensity profile along the topmost layer. Bottom-left inset: top view of the DFT-optimized structure showing H adsorption at the Cu-Pt hollow sites. Upper-left inset: simulated HRTEM and the intensity profile along the topmost layer. (b) HRTEM image of the (410) surface showing the Pt segregation to step edges and their next nearest neighbors. Bottom-left inset: DFT-optimized structure showing H adsorption at the hollow sites (terraces) and bridge sites (steps). Upper-left inset: simulated HRTEM image of the stepped surface and the intensity profile of the topmost layer of the terrace. Blue, silver and pink spheres represent Cu, Pt and H, respectively.

References

- [1] C.R. Li., et. al., *Phys. Chem. Chem. Phys.* 22, 3379 (2020)
- [2] Shen, Y.G., et. al., *Surf. Sci.* 406, 23 (1998)
- [3] Greeley, J., et. al., *J. Phys. Chem. B.* 109, 3460 (2005)
- [4] Yasumori, I., et. al., *Jpn. J. Appl. Phys.* 13, 485 (1974)
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