

Nanoscale control of self-diffusion processes in bimetallic alloys to tailor surface properties

Achieving control of the nanoscale structure of binary alloys to design novel materials with specific properties may yield to improved reaction rates and selectivity in catalysis, tailored magnetic behavior in electronics, and controlled growth of nanostructured materials. Complex self-diffusion mechanisms determining these key properties close to the surface of a Ni-Cu system can be controlled by finely tuning the relative concentration of the alloy constituents, thus tailoring the material functionality and providing a clear explanation for previously observed effects.

In general, achieving control of the nanoscale structure is of paramount importance for the design of novel materials with specific properties, leading to, for example, improved reaction rates and selectivity in catalysis (reduction of carbon dioxide), tailored magnetic behavior in electronics, and controlled growth of nanostructured materials (graphene). For binary alloys, the composition of the material in the surface region is of crucial importance in determining key properties, and is determined by complex self-diffusion and segregation mechanisms of the different atomic components. Close control of these processes would make tailoring of the material functionality possible by finely tuning the relative concentration of the alloy constituents. By means of a combined experimental and theoretical approach, we have studied this issue for the Ni-Cu system, where the above mechanisms were shown to be mostly defined by kinetic rather than energetic effects.

The processes taking place at the Ni/Cu(110) surface have been followed by high-energy-resolution

x ray photoelectron spectroscopy experiments performed at the SuperESCA beamline. Starting from a Ni coverage of 0.75 ML, XPS was used to monitor, at selected fixed temperatures, the real time evolution of the Cu and Ni core levels (Fig. 1). After preparation of the Ni ad-layer, the sample temperature was suddenly raised to the selected target value, following a step-like profile. A spectroscopic

“movie” of the segregation process was then obtained by analyzing the dependence of the core level signal intensities as a function of time. Due to the finite inelastic mean free path of the photoemitted electrons, upon diffusion of Ni atoms into the Cu bulk the Ni signal is screened by the atomic layers above. In parallel, as the Cu concentration at the surface increases, the Cu signal intensity raises. The Ni and

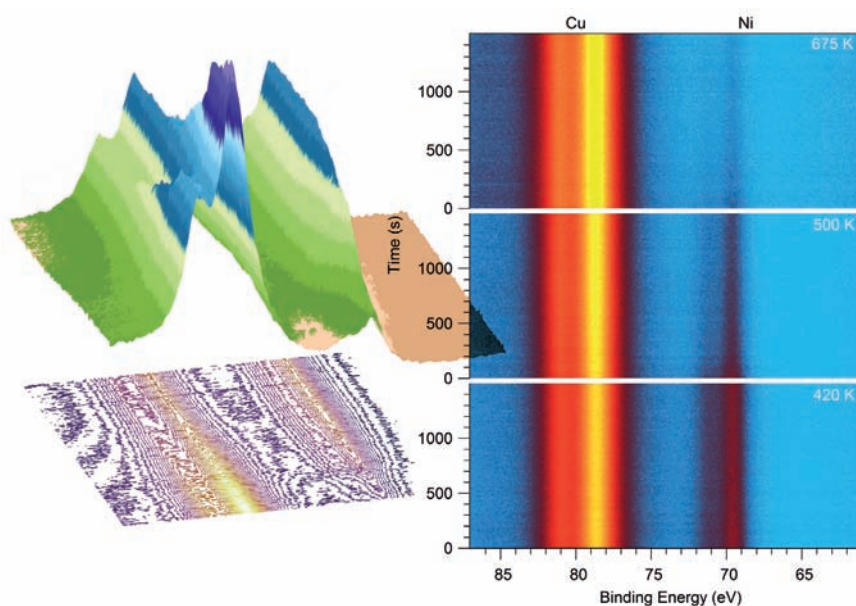


Figure 1. Bi-dimensional maps of the evolution of the photoelectron spectroscopy signal from the Cu and Ni 3p core levels upon Ni and Cu segregation as a function of binding energy and time. In the right panel, data are reported for experiments at three selected temperatures.

Cu signal intensities are therefore related to the composition profile of the sample in the direction perpendicular to the surface. In order to obtain quantitative information, we modeled the diffusion process and optimized a set of parametric rate equations to fit the experimental intensities. Ni segregation energy barriers of increasing height were obtained when going deeper into the Cu(110) sample (from 1.2 to 2.0 eV, moving from the first layer to the bulk). In parallel, Density Functional Theory (DFT) ab-initio calculations modeled the most relevant processes, providing from the theory side diffusion and segregation energy barriers (Fig. 2). On the basis of the obtained information it was concluded that: (i) in the absence of a gas phase chemical potential contribution, there is an energy gain when Ni penetrates Cu from the surface to the second layer, whereas no further gain is obtained in going to deeper layers; (ii) the energy barriers that have to be overcome for diffusion into deeper layers are high with respect to the system temperature under realistic reaction conditions for carbon dioxide reduction on a Ni-doped Cu single crystal ($T < 550$ K), thus indicating the relevance of kinetic limits to the

processes; (iii) these barriers vary significantly by changing the Ni concentration, while the energies of the final configurations remain comparable (Fig. 2a with respect to Fig. 2b). This is a key point, showing that the segregation behavior determined by kinetics and ultimately by the Ni–Ni interaction, can be directly controlled by a fine tuning of the

Ni coverage. Observations about carbon dioxide heterogeneous catalytic conversion to methanol (in a $\text{CO}_2 + \text{CO} + \text{H}_2$ stream) on a model Ni/Cu(100) catalyst at ambient pressure conditions indicate that controlled nickel doping of the copper surface in the sub-monolayer range accounts for an increase in the turnover frequency up to a factor of 60.

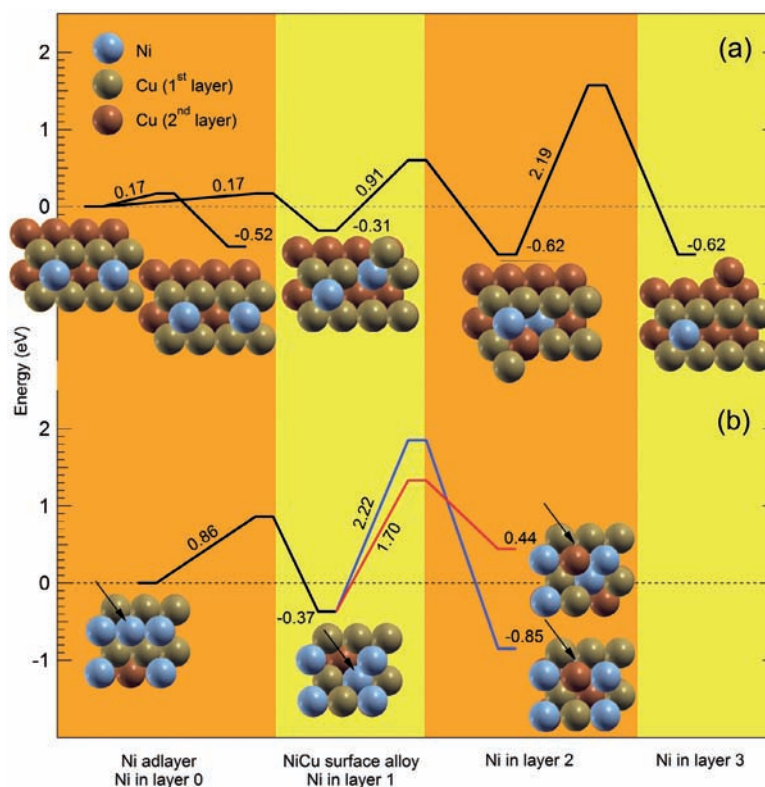


Figure 2. Alloying paths and barriers calculated by means of ab-initio methods (DFT). (a) decomposition of a Ni ad-dimer. (b) bulk-diffusion of a Ni ad-atom detaching from a 5/6 ML Ni ad-island.

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