Ab-Initio Thermodynamics Of Alloy Surfaces: From The Local Atomic Structure To Substitutional Ordering Of One Million Atoms

S. Müller

University Erlangen-Nürnberg, Lehrstuhl für Festkörperphysik, Staudtstr. 7, D-91058
Erlangen
e-mail: s.mueller@fkp.physik.uni-erlangen.de

In recent years the combination of density functional theory (DFT) with methods from statistical physics has experienced to study in particular surface processes with a delicate temperature dependence as e.g. catalytic processes (e.g. [1]) or surface segregation (e.g. [2]). The latter describes the deviation of the stoichiometry in the surface region from that of the bulk. This surface segregation takes place in many metal alloys and is controlled by the chemical equilibrium between the near surface-layers and the bulk. Consequently, a successful theoretical description of this phenomenon demands a consideration of both, bulk and surface properties leading to model slabs consisting of hundreds, if not thousands of atoms. Moreover, in general first-principles methods based on DFT cannot take configurational enthalpies into account and, consequently, are not able to describe the segregation of atoms. A third obstacle to be overcome is the complex energetics of the near surface layers. Different from the bulk, pair- and multibody interactions between atoms are layer dependent leading to a huge number of parameters which must be determined to model
segregation processes.

In this contribution, we discuss recent developments, the possibilities and limitations to study surface segregation in metal alloys based on first-principles methods, i.e. without the input of any empirical parameter. In this context, we will present to the best of our knowledge for the first time a DFT-based approach considering both, the layer-dependent interactions and the temperaturedependent configurational entropy. This allows to study segregation profiles and ordering phenomena of geometrically fully relaxed metal alloy surfaces (3-dimensional).

DFT calculations [3] of alloy surfaces can be used to construct a surface phase diagram for the alloy's near-surface region [4]. For this, we first describe the energetics of a certain bulk concentration by applying first-principles calculations combined with cluster-expansion (CE) techniques [5]. This allows the treatment of large unit cells necessary to access arbitrary bulk concentrations. Second, we derive an equation for the surface formation enthalpy, which depends on both, the ordering and the concentration at the surface. Their energetics is described by DFT calculations
for a surface slab and the chemical potentials of the different species involved. Hereby, equilibrium with the bulk must be considered, by which the energetics of the bulk calculated in the first step gets involved. Third, the chemical potential of the antisites within the surface slab is transformed to the temperature scale yielding the surface phase diagram in the (T; x) plane. As one first example, this concept will be applied to the segregation of Co antisite atoms in the (100) surface of CoAl.

In order to access short-range order the CE is extended to surfaces and combined with Monte- Carlo simulations [6]. For this, we have to consider that the symmetry at the surface is reduced as compared to the bulk. Consequently, the number of geometrically different figures, for which effective interactions are constructed, will increase. For this reason, a larger number of input-structures are needed to stabilize the surface interactions compared to the bulk. It is however possible to circumvent part of this

problem by treating the surface interactions as correction of the bulk interactions. Since energies are additive, we can write

$$\Delta H_f^{CE} = \Delta H_f^{Vol} + \Delta H_f^{Surf}$$

Since most segregation profiles are restricted to a very small number of surface layers, a real-space presentation can be applied for the surface part [7]. The advantage in treating the surface interactions as "perturbation" of the bulk interactions comes from the fact that the DFT calculations for different surface terminations and segregation profiles must not consider an infinite bulk reservoir. We only have to make sure that the DFT slab-model is thick enough to ensure that the center layer of the slab is bulk like. This access allows also to study alloy surfaces which do not show long-range order at all, as e.g. Pt-Rh alloy surfaces [8].

Since our approach gives access to mesoscopic systems, it allows for a quantitative prediction of short-range order and therefore, for a direct comparison with STM studies. The concept can also be applied to epitaxial _lms, the morphology of islands, or adsorption systems.

References:

[1] K. Reuter and M. Sche_er, Phys. Rev. B 65, 035406 (2001).
[2] V. Blum, L. Hammer, Ch. Schmidt, W. Meier, O. Wieckhorst, S. Müller, and K. Heinz, Phys. Rev. Lett. 89, 266102 (2002).
[3] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169; 1996 Comput. Mater. Sci. 6 15
[4] O. Wieckhorst, S. Müller, L. Hammer, and K. Heinz, subm. to Phys. Rev. Lett.
[5] J. M. Sanchez, F. Ducastelle, D. Gratias, Physica A 128, 334 (1984).
[6] S. Müller, J. Phys.: Condens. Matter 15, R1429 (2003).
[7] R. Drautz, H. Reichert, M. Fähnle, and H. Dosch, J. M. Sanchez, Phys. Rev. Lett. 87, 236102-1 (2001).
[8] E. Platzgummer, M. Sporn, R. Koller, S. Forsthuber, M. Schmidt, W. Hofer, and P. Varga, Surf.Sci. 419, 236 (1999).2