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COMMENT

Comment on the surface segregation in alkali-metal alloys

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Abstract. The models of surface segregation of the atoms in alkali-metal alloys are briefly commented on.

The phenomenon of surface segregation, which has been observed experimentally in many binary alloy systems, also attracts quite a lot of theoretical interest. Recently several authors [1–3] have tried to treat this problem by applying the density functional formalism and the uniform background model (jellium). Each of these papers extends the theory for a one-component metallic surface to the case of a two-component system.

To go beyond the jellium model, Kiejna and Wojciechowski [1] have applied the virtual crystal approximation for the bulk and performed the calculations for the alkali-metal alloys in the way analogous to the calculation of face-dependent surface properties of clean metal surfaces [4]. Although the surface segregation was not the main subject of our calculation [1], it enabled us to see if surface segregation in this type of alloy is possible.

Lang's double-step jellium model for metallic adsorption [5] was employed by Yamauchi [2] to represent the positive charge density on the surface of an alloy with a segregating surface component. The variational electron density profile was represented by an analogous function to that in our paper [1]. The energy of a system was minimised with respect to a variational parameter for different values of height and thickness of the positively charged slab of jellium representing the segregating component. Yamauchi performed the calculations for a number of binary solutions of a substitutional type and has formulated the following rule: atoms of the component having the larger Wigner–Seitz radius r_s segregate to the surface.

Recently Digilov and Sozaev have presented a model [3] which includes elements of the approach of Yamauchi [2] (double-step jellium) and of ours [1] (inclusion of the lattice terms to the surface energy functional). They performed calculations for Na–K alloy and found that ‘... contrary to the model of paper [1] in the whole range of solute/solvent atoms concentration surface segregation of potassium occurs’. Because potassium is characterised by the larger Wigner–Seitz radius, its segregation to the surface of a Na–K solution is in agreement with Yamauchi's rule and *does not* contradict our results.

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It is a purpose of this comment to clear up this point and to demonstrate that our calculations agree both with those of Yamauchi [2] and Digilov and Sozaev [3].

In our search for surface segregation we considered [1] a simple model in which the core radius of the model potential of the ions in the outermost atomic layer could vary to minimise the surface energy of an alloy. Thus the surface energy was minimised with respect to two parameters: the electron density decay parameter β and the pseudopotential core radius r_{c1} in the last atomic layer. In the case of segregation we expected to find a minimum with respect to r_{c1} in the surface energy curves, i.e. we did not expect a complete segregation but only a partial enrichment of surface composition by one of the constituents.

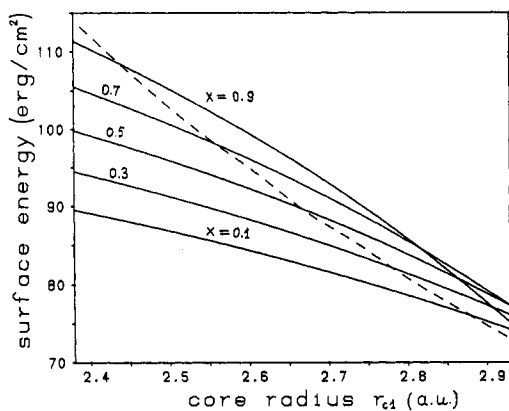


Figure 1. Surface energy plotted against the pseudopotential core radius in the outermost atomic layer of the (110) K_xCs_{1-x} surface for different concentrations x of the constituents. The broken curve shows surface energy as a function of the concentration of the alloy constituents for the case without segregation (the dependence on the concentration of the constituents of the alloy is given through the value of r_{cx} , where $2.38 \leq r_{cx} \leq 2.93$).

In figure 1 we have plotted typical curves of the surface energy minimum with respect to the parameter β as a function of the pseudopotential core radius r_{c1} for the (110) surface of K-Cs solid solution. There is no minimum in these curves which vary monotonically between r_{cA} and r_{cB} , where r_{cA} and r_{cB} represent the pseudopotential core radius of K and Cs atoms, respectively. However, the surface energy is the lowest when $r_{c1} = 2.93$, which corresponds to the core radius of the Cs ion. Therefore one can conclude that for this system it is always caesium atoms which segregate to the surface and complete segregation occurs. For the sake of comparison, in figure 1 we have also drawn the surface energy as a function of the concentration of the constituents in the bulk alloy (broken curve) for the case without segregation, i.e. for $r_{c1} = r_{cx}$, where r_{cx} is the core radius of a pseudo-ion in the bulk alloy determined for a given concentration x in the virtual crystal approximation [1]. Note that r_{cx} varies similarly to r_{c1} between 2.38 (pure K) and 2.93 (pure Cs). The lowering of the surface energy in the surface layer of alloy is the result of the smoothing of the surface electron density profile with the increase of the concentration of the constituent which has the larger r_s . A similar trend was observed for other alkali-metal alloys where, in accordance with Yamauchi's report, the atoms of the constituent which has the larger Wigner-Seitz radius enrich the alloy surface. This was in fact our conclusion, but since we

expected a partial enrichment we have concluded only that it is always one of the components that minimises the surface energy. It appears that this is confirmed by thermodynamical considerations which suggest that the binary alloy surface should consist of one type of atoms only (see [2] and references therein). Unfortunately we overlooked the *lower average electron density* characterising an alkali solid, and wrote improperly that it is always the lighter constituent of the alloy which enriches the surface, instead of noting that these are the atoms of the element characterised by the lower average electron density $\bar{n} = 3/(4\pi r_s^3)$. This misunderstanding becomes evident if one compares our statement in [1]: '... since throughout the group of alkali metals the lighter is the element the lower is its surface energy (compare table 2)' with the contents of table 2 in [1]. As one can see the lower the average electron density of a metal (the larger the Wigner-Seitz radius r_s), the lower its surface energy is. It follows that the alloy surface with the segregated atoms of the component characterised by the larger Wigner-Seitz radius becomes lowest in energy.

In conclusion, we have cleared up some misunderstanding of our previous work [1]. The above mentioned different models of surface segregation predict accordingly that it is always the component with the larger Wigner-Seitz radius which segregates to the surface of binary alkali-metal alloys. It implies that the driving force for the surface segregation is the reduction in the surface energy of the segregated alloy.

Acknowledgments

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