

Surface and Subsurface Segregation of Co Antisite Atoms in CoAl

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In order to minimize the total energy of a disordered alloy crystal, those atoms segregate to the surface, which own the lower surface energy. In ordered systems, this energy gain has to be paid by the energy necessary to create antisite atoms in the bulk and at the surface. In strongly ordering systems, i.e. such with a large formation enthalpy, this energetic balance turns out to be unfavourable and hence, no segregation is observed in the ideal stoichiometric case. However, the situation changes completely, when the crystal is even only slightly off-stoichiometric. Then, antisites atoms are already present in the bulk and may in fact lower the energy by accumulation at the surface, sometimes even at the expense of replacing atoms with lower surface energy. In that sense, this type of “antisite segregation” is a reversal of the “regular” segregation process. It has recently been postulated on theoretical grounds [1] and independently found by LEED experiments and quantitative analyses for a CoAl(100) surface and explained on the basis of DFT calculations [2].

In the bulk phase diagram of Co-Al, the B2 (= CsCl) phase region extends remarkably into the Co-rich side with the predominant defect type in this range being the Co antisite atom [3]. Moreover, the intermetallic compound CoAl is strongly ordering ($\Delta H_f = -54,2$ kJ/mol [4]) and thus is an excellent candidate for the investigation of the site-dependence of “antisite segregation”. We compare experimental results as well as theoretical predictions for the three low-index surface orientations (111), (100) and (110). While the first two surfaces are nominally terminated by a pure Al layer with an alternating layer stacking below, the layers of the (110) surface are all of mixed stoichiometry. In all cases, the concentration of Co antisites in an extended subsurface region, which virtually acts as a “reservoir”, can be tuned experimentally by ion sputter-induced Al-depletion and subsequent annealing at various temperatures.

In case of the (100) surface segregation makes Co antisite atoms first accumulate in the outermost layer. However, due to repulsive interactions within this layer accompanied by attractive interactions in vertical direction, subsurface segregation into the third layer (which is the next Al layer) comes into play. Eventually, this subsurface layer becomes completely filled, while the top layer still remains chemically mixed.

The (111) surface, in contrast, is a rather open surface with atoms in the top three layers being undercoordinated. For the very first layer no antisite segregation at all is observed within the investigated off-stoichiometry range. In contrast, the third layer becomes practically completely filled by Co antisite atoms. For higher concentrations within the antisite reservoir there is experimental evidence for accumulation in even deeper layers.

For the (110) surface there are also no hints for antisite segregation into the first layer. However, earlier investigations [5] found again evidence for subsurface segregation, here substituting Al atoms of the second layer.

In conclusion, the segregation behaviour is controlled by a delicate competition between surface and antisite energy, whereby in most of the cases under investigation nature realizes subsurface accumulation as a compromise. This seems to be favoured by the fact that around subsurface antisites more geometrical relaxations are possible, so that the total energy can be reduced without significant loss of surface energy. Only in case of the (100) surface, where the next available sites in the third layer are already bulk-like, antisite segregation first proceeds towards the outermost layer.

References

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