

Comment on Chemisorption Induced Segregation of Impurities at Transition Metal Surfaces

The results obtained by Bernasek and Staudt (8) for molybdenum are in agreement with our observations in the case of Pd, Pt, Cu, Ni (1, 2) and give one more evidence that the sulfur segregation from the bulk to the surface of a metal single crystal caused by hydrogen chemisorption is a very common phenomenon. The role of hydrogen adsorbed on the surface and absorbed in the bulk is difficult to separate, since absorption is always accompanied by adsorption which is its precursor process.

Reporting our results on Pd (100) (1) we were of the opinion that in that particular case the absorbed hydrogen could influence the segregation of sulfur because of the special ability of palladium to dissolve hydrogen. To verify this hypothesis we have studied several metals with different characteristics of behavior with respect to hydrogen: Pt (100) and Cu (100) in addition to Pd (100). Taking into account all the experimental evidences we could conclude that the hydrogen adsorption alone is a driving force which induces sulfur segregation from the bulk to the metal surface (2). The influence of hydrogen absorbed in the bulk has not been ascertained univocally up to now.

As concerns the study by Bernasek and Staudt (8) the authors suggest the close correspondence between the sulfur segregation and the solubility of hydrogen in molybdenum. However, the authors do not take into consideration the adsorption of hydrogen on molybdenum. As it was shown by Abon and Teichner (3) hydrogen desorbs completely from molybdenum sur-

face between 1100 and 1400 K, and this phenomenon can be responsible for lowering segregation of sulfur starting from the temperature of 1100 K.

Bernasek and Staudt mention (8) the influence of the dissolution of H₂ in metal on the rate of sulfur segregation. However, it does not seem possible to observe purely kinetic effects in such a kind of experiments.

In the studies of surface segregation the thermodynamical and kinetic aspects are very difficult to separate. On the thermodynamical basis one can expect that the effect of thermal segregation of one component of an alloy (or an impurity) *in vacuo* should decrease with increasing temperature (4). But for the rate of diffusion, which controls the kinetics of segregation, just the reverse is true. That is why at lower temperatures the system may be distant from equilibrium and the increase of segregation is due to kinetic effect. Therefore, the plot of the concentration of the segregated element (e.g., sulfur) against the temperature shows a maximum. Mróz *et al.* (5) observed such behavior in the Ni-S system. Thus from both the thermodynamical and the kinetic points of view the shape of the curve in Fig. 2 of Ref. (8) is to be expected even without adsorption of hydrogen. In fact the thermal segregation of sulfur *in vacuo* was observed for polycrystalline molybdenum (6) and Mo (112), (110), and (100) (7).

As to the remark of Bernasek and Staudt concerning the diffusion of sulfur from our molybdenum holder onto the palladium sample, the effect does not seem to be re-

sponsible for the presence of sulfur on the surface since for various metals we have observed the different shapes of curves representing the surface sulfur concentration as a function of the temperature (2). Moreover, our sample hardly touches the holder so it would not be the diffusion process but rather unprobable "jumping" of sulfur from the holder onto the sample.

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