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Adsorption and segregation of sulphur, and its influence on the carburization and nitrogenation of iron and steel*

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The surface segregation of sulphur on iron was investigated by A.e.s. on iron polycrystals in the temperature range 700–1100 °C. Strong surface segregation occurs even at low bulk concentrations of 2–20 μg/g. The enthalpy of segregation for S(dissolved) = S(adsorbed) is about −165 kJ/mole S. By l.e.e.d. studies at 750 °C, ordered adsorption structures were observed on iron single crystal surfaces.

In the segregation studies the equilibrium sulphur activity, a_S, was determined by the concentration of dissolved sulphur. The results were correlated with the surface reaction kinetics in the carburization and nitrogenation of iron in the presence of adsorbed sulphur. These studies were performed in a flow apparatus at atmospheric pressure, the sulphur activity being established by the H_2S/H_2 ratio in the gas atmosphere. The effect of adsorbed sulphur was studied for the reactions $CH_4(g) = C(\text{dissolved}) + 2H_2(g)$ and $N_2(g) = 2N(\text{dissolved})$ by a resistance relaxation method on thin iron foils at 800–900 °C. Even at bulk concentrations of about 0.1 μg/g S, the surface reactions were strongly retarded. Carbon and nitrogen transfer can only occur on reaction sites free of adsorbed sulphur. It can be seen from the kinetics that two sites are needed for the dissociation of N_2 but one site is sufficient for the decomposition of CH_4. From the reaction kinetics, the adsorption isotherm for sulphur adsorption and segregation at 850 °C could be derived.

The effect of adsorbed sulphur on the surface reaction kinetics can be used as a barrier against carbon or nitrogen transfer during heat treatment. The presence of sulphur-containing compounds during annealing steel sheet in N_2–H_2 atmospheres at 650–700 °C will suppress decarburization and nitrogenation or denitrogenation. The presence of sulphur on a steel surface stops the carbon deposition from CO by a Boudouard-type reaction and also the formation of graphite on the surface from the decomposition of metastable cementite in the bulk. In ethylene furnaces, additions of sulphur-containing compounds to the feedstock have proved advantageous in the protection of high-alloy steel tubes from carburization. This effect has been confirmed by studies of the carburization, i.e. internal carbide formation, with Incoloy 800 at 1000 °C in strongly carburizing CH_4–H_2–H_2S atmospheres. By increasing the ratio H_2S/H_2 from 10^{-6}, the carburization was progressively retarded. The minimum corrosive attack occurred at about $H_2S/H_2 = 10^{-4}$, while at higher H_2S contents simultaneous carburization and sulphidation were observed. This protective effect may be important for application in petrochemistry, coal gasification and in the high temperature nuclear reactor.

Bibliography (Grabke *et al.*)

Grabke, H. J., Paulitschke, W., Tauber, G. & Viefhaus, H. 1977 *Surface Sci.* **63**, 377–389.
Grabke, H. J., Paulitschke, W. & Srinivasan, S. R. 1977 In *Reactivity of solids* (ed. J. Wood *et al.*), pp. 55–61. Plenum Press.
Grabke, H. J., Petersen, E. M. & Srinivasan, S. R. 1977 *Surface Sci.* **67**, 501–516.
Tauber, G. & Grabke, H. J. 1978 *Ber. BunsenGes. phys. Chem.* **82**, 298–302.

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