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Chemisorption-Induced Sulfur Segregation from the Bulk to the Surface of Pt(100) and Cu(100)

In a previous paper we have reported the hydrogen-induced surface segregation of sulfur present as an impurity in palladium (*1*). In order to find out whether the phenomenon is of a general character we have carried out analogous studies on Pt(100) and Cu(100). These metals were chosen because of the differences in their behavior with respect to hydrogen (*2*). Palladium is known to adsorb and absorb hydrogen readily; platinum dissolves hydrogen to a lesser extent although it does adsorb this gas very well; copper is a poor adsorbent and absorbent of hydrogen.

The Auger electron spectroscopy (AES) apparatus and the method of investigation were described earlier (*1*). The only difference in the experimental procedure was that after the exposure of the metal sample to hydrogen at a given temperature the gas was pumped out and the sample was cooled *in vacuo* to room temperature. The hydrogen interaction with the metal surfaces resulted in the appearance of the sulfur peak in the Auger electron spectra. No other changes were seen in those spectra during the experiments.

The dependence of surface concentration of sulfur on exposure to hydrogen $p_{H_2} = 1.6 \times 10^{-2}$ Pa (1 Pa = 1 N m^{-2} = 7.5×10^{-3} Torr) at various temperatures for Cu(100) is shown in Fig. 1. The peak-to-peak ratio S 155 V/Cu 113 V has been taken as the measure of the surface concentration of sulfur. The surface concentration of sulfur segregated from the bulk crystal increased with exposure to hydrogen. The influence of hydrogen on the extraction of sulfur to the surface was much less pronounced for copper than for platinum or for palladium. However, it should be pointed out that the absolute height of the sulfur peak was much smaller in the AES spectra of Cu(100) than in the case of Pd(100) and Pt(100). It was observed for samples before the cleaning procedure and after their thermal treatment *in vacuo* as well.

The effect of the temperature at which the samples were exposed to hydrogen is shown in Fig. 2. The experiments were carried out in the temperature range 298–773 K. The curve obtained previously for Pd(100) is also shown for comparison. In the case of Pd(100) and Pt(100) the extent of the sulfur segregation increased with temperature. However, the effect was quite different for Cu(100). At higher temperatures it was less pronounced and finally above 630 K hydrogen did not extract sulfur any more.

It should be added here that the purely thermal segregation (i.e., *in vacuo*) of sulfur to the surface of the metals investigated has not been observed below 770 K. When discussing previously the surface segregation of sulfur induced by hydrogen chemisorption on Pd(100), we suggested that the high solubility of hydrogen in palladium could be related to the phenomenon. However, the additional data now obtained for the systems Pt(100)–H_2 and Cu(100)–H_2 have supplied evidence that the adsorption of hydrogen on the metal surface is a sufficient condition. The relationships S/Me = $f(T)$ for Pd(100) and Pt(100) are

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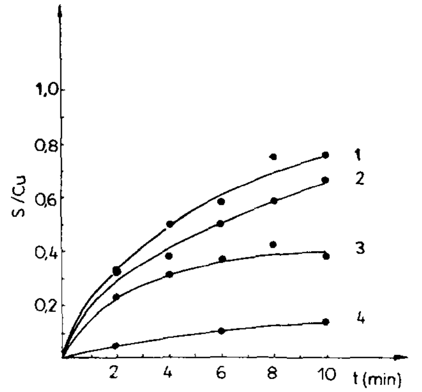

FIG. 1. The S/Cu peak-to-peak ratio as a function of exposure to hydrogen, $p_{H_2} = 1.6 \times 10^{-2}$ Pa, at different temperatures: (1) room temperature, (2) 410 K, (3) 490 K, and (4) 610 K.

similar since both these metals are good adsorbents for hydrogen although their hydrogen absorption abilities are different. The heats of adsorption of hydrogen are 88 kJ mole^{-1} (*3*) and 70 kJ mole^{-1} (*4*, *5*) for Pd(111) and Pt, respectively. Copper is a poor adsorbent for hydrogen; the heat of adsorption of hydrogen on Cu is about 40 kJ mole^{-1} (*6*, *7*). The amount of hydrogen adsorbed on copper rapidly decreases with increasing temperature; therefore, the effect of hydrogen on sulfur segregation disappears at higher temperatures.

As in the case of Pd(100), in addition to AES measurements we have carried out by low energy electron diffraction observations of the changes in surface structure on exposure to hydrogen. The clean surface of Pt(100) displayed the well-known (5 × 1) structure. Exposure of the sample to hydrogen under a pressure of 1×10^{-2} Pa at 873 K caused the appearance of the (2 × 2) structure. The same structure was observed earlier by Morgan and Somorjai (*8*) in similar conditions of temperature and hydrogen pressure. Since AES analysis of the surface of the Pt(100) sample, carried out

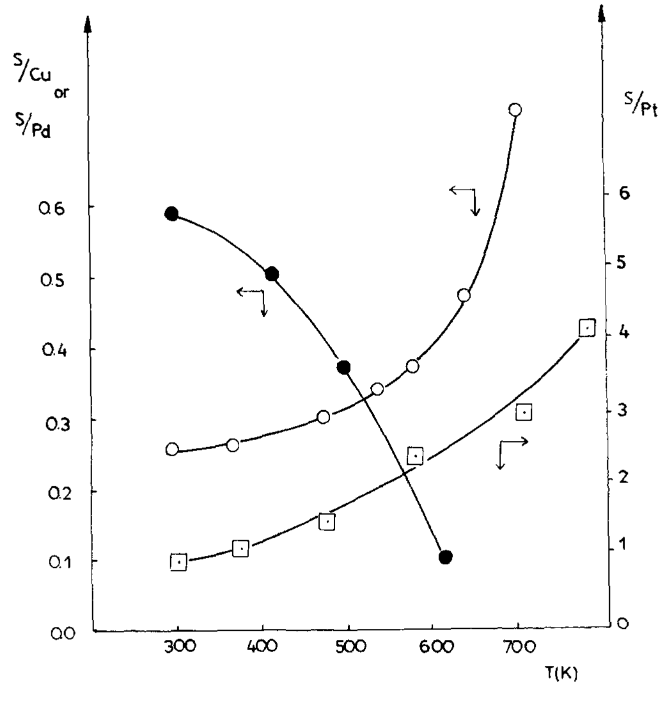

FIG. 2. The effect of heat treatment in hydrogen, $p_{H_2} = 1.6 \times 10^{-2}$ Pa, on the surface concentration of sulfur for Pt(100) ⊡, Cu(100) (●), and Pd(100) (○). To calculate the S/Me ratios the following Auger transitions were used: S-155 V ($L_{2,3}M_1M_1$); Pt-238 V ($N_5N_{6,7}O_{4,5}$); Cu-113 V($M_1M_{4,5}M_{4,5}$); Pd-333 V ($M_{4,5}N_{4,5}N_{4,5}$).

in our studies after the exposure to hydrogen, showed the presence of sulfur on the surface, we suggest that the observed (2 × 2) structure was due to the presence of sulfur and not to hydrogen on the surface of platinum. As a result of further exposure of the sample to hydrogen, the $p(2 \times 2)$ structure changed to $c(2 \times 2)$. Simultaneously the height of the sulfur Auger peak S 155 V increased. Our hypothesis is additionally supported by the fact that a similar sequence of diffraction patterns has been recently observed by Heegemann *et al.* (*9*) during adsorption of sulfur on the surface of Pt(100).

It appears that the chemisorption-induced sulfur segregation from the bulk to the surface of a metal (even very pure metal) is a very common phenomenon. It should, therefore, be borne in mind that this effect may occur in many different reactions catalyzed by metals if hydrogen is one of reactants.

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