

## LETTERS TO THE EDITORS

Chemisorption Induced Segregation of Impurities at  
Transition Metal Surfaces

A recent study by Szymerska and Lipski (1) of chemisorption induced sulfur segregation at the surface of a palladium single crystal has indicated that exposure of the palladium sample to hydrogen induces a migration of bulk sulfur to the palladium surface. We would like to report a similar observation of chemisorption induced bulk sulfur segregation on a molybdenum surface.

In the course of cleaning a molybdenum (100) surface prior to LEED-AES studies, we observed an increase in the sulfur (150 eV) peak after heating the sample in hydrogen in order to reduce a surface oxide layer. Ion bombardment removed the sulfur peak which could be regenerated by further exposure to hydrogen. Ion bombardment to remove the sulfur followed by annealing in vacuum for the same time and at the same sample temperature as for hydrogen exposure did not regenerate the sulfur (150 eV) peak. Auger spectra corresponding to the treatments described above are shown in Fig. 1.

The effect of sample temperature on the chemisorption induced segregation of sulfur on the surface of the molybdenum sample is indicated in Fig. 2. The ratio of the sulfur Auger peak at 150 eV to a molybdenum Auger peak at 185 eV after 3 hr exposure to  $H_2$  at  $8.0 \times 10^{-3}$  Pa is plotted versus the temperature of the surface during hydrogen exposure. This quantity is proportional to the rate of sulfur segregation at the molybdenum surface (slope of a plot of sulfur

peak height vs time) at the stated pressure and sample temperature. Equilibrium sulfur peak height is attained after much longer exposures ( $\sim 10$  hr in the 1000 K case of Fig. 1). It can be seen that the ratio increases with increasing temperature to about 1000 K and then decreases with increasing temperature. Also plotted in Fig. 2 is the solubility of  $H_2$  in molybdenum which exhibits a similar behavior as a function of temperature (2).

Two conclusions can be stated in light of the present observations and those of Szymerska and Lipski (1). The first is that  $H_2$  chemisorption induced segregation of bulk sulfur may be directly related to the solubility of  $H_2$  in sulfur contaminated transition metals. The explanation of this effect offered by the authors of Ref. (1), is based on the solubility of  $H_2$  in palladium. They ascribe a "hindering action in sulfur diffusion" to the dissolved hydrogen, which is greater at low temperatures due to the greater solubility of  $H_2$  in palladium at low temperatures. As the temperature is increased, less  $H_2$  is dissolved, and more sulfur diffuses to the surface, according to these authors. If this explanation were valid, it would seem that the most rapid segregation should occur when the  $H_2$  exposure was lowest. This is in fact not the case in either Szymerska and Lipski's work or the present observations.

Perhaps a more reasonable explanation lies in the close correspondence between

the rate of sulfur segregation at the surface as a function of temperature, and the solubility of hydrogen in molybdenum as a function of temperature. The dissolution of  $H_2$  in the metal appears to be very closely related to the rate of sulfur segregation. As the solubility increases, the segregation

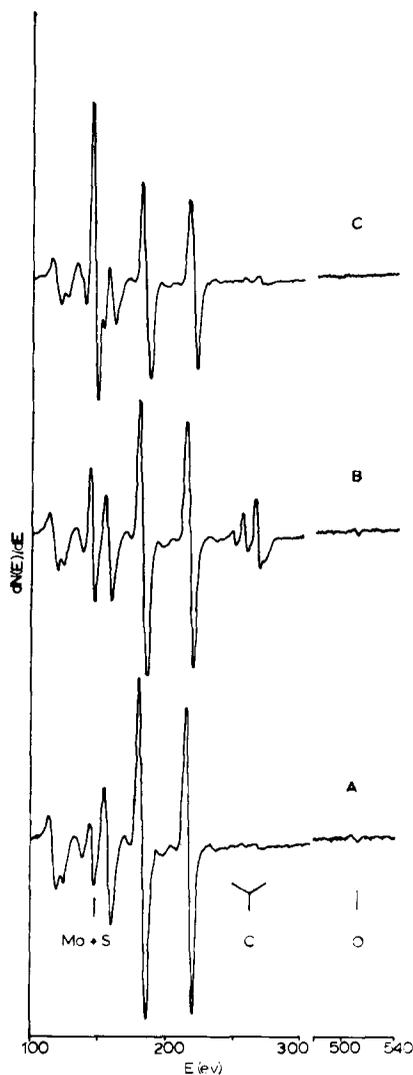


FIG. 1. Auger spectra of Mo(100). (A) After brief ion bombardment; (B) after heating in vacuum ( $7.0 \times 10^{-8}$  Pa) at  $1000^\circ\text{K}$  for 10 hr; (C) after heating in  $8.0 \times 10^{-3}$  Pa  $H_2$  at  $1000^\circ\text{K}$  for 10 hr. Spectrometer conditions:  $E_p = 1.5$  KeV,  $E_m = 2$  eVp-p,  $I_p = 30$   $\mu\text{A}$ .

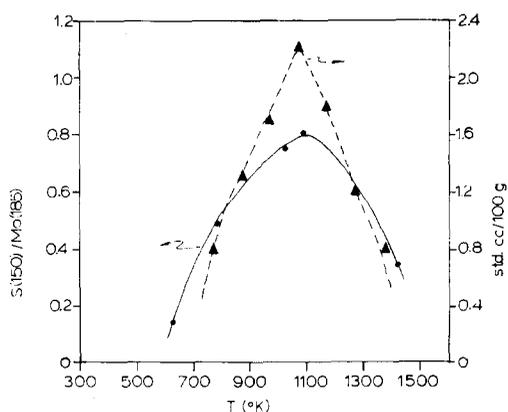


FIG. 2. (●) Ratio of sulfur Auger peak at 150 eV to molybdenum Auger peak at 185 eV plotted vs temperature of sample during hydrogen exposure. Peak at 150 eV has been corrected for the molybdenum transition at 150 eV which overlaps the sulfur peak, by subtracting the peak height at 150 eV of the clean Mo(100) spectrum [obtained by the treatment corresponding to (A), Fig. 1], from the  $H_2$  exposure spectra. (▲) Solubility of  $H_2$  in molybdenum vs sample temperature. Solubility given in cubic centimeters at STP absorbed/100 g of sample. Data taken from Ref. (2).

rate increases, and as the solubility decreases with increasing temperature, the segregation rate decreases. This close correspondence does not seem to indicate a "hindering action" for  $H_2$  dissolved in the metal. It should be pointed out that the possibility of sulfur segregation on the molybdenum mounting strip, with subsequent diffusion to the palladium sample, cannot be excluded in the work of Ref. (1). This possible effect would complicate the interpretation of the results of Ref. (1).

The second conclusion arising from this work is to again emphasize the need for *in situ* verification of the impurity content of a transition metal surface after even an "established" cleaning procedure. The reduction of transition metal surfaces in hydrogen is a commonly accepted technique for preparing a clean surface, and as is seen from the above discussion, can result in further contamination of the surface under study.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Szymerska, I., and Lipski, M., *J. Catal.* **41**, 197 (1976).

2. Smithells, C. J., "Metals Reference Book," 4th ed., p. 605. Butterworths, London, 1967.

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