Switchable mirrors for visualization and control of hydrogen diffusion in transition metals

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We show that the switchable mirror material YH2 can be used both as an indicator to monitor and as an agent to control hydrogen diffusion in thin films. The applicability of the optical-indicator technique is demonstrated for VH3 thin films. The diffusion coefficient is typically 10−3 cm2/s at concentrations around 0.7 H/V at temperatures between 373 and 473 K. Deposition of a layer of Y on V makes it also possible to tune the effective hydrogen mobility via the V/Y thickness ratio. This can be used for investigation of hydrogen diffusion waves in laterally structured objects.

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One of the striking properties of hydrogen in metals is its large mobility. Already at room temperature the H diffusion coefficient can be as high as 10−5 cm2/s, i.e., a value almost comparable to diffusion in liquids. A review of experimental data and techniques used so far to measure hydrogen diffusivity in bulk samples is given by Alefeld and Völkl.1 Most of these methods are not applicable to thin films as they are either hampered by the influence of the substrate (e.g., in Gorsky effect) or by the rather small volume of the film (e.g., in quasielastic neutron scattering). Consequently, relatively little is known about hydrogen diffusion in thin metallic films and multilayers. The understanding and manipulation of hydrogen transport through films is, however, important for the control and optimization of coatings and thin-film devices such as hydrogen detectors,2,3 metal-hydride switchable mirrors4,5 or tunable magnetic elements.6,7 Recently den Broeder et al.8 presented an optical method to monitor the lateral migration of hydrogen in Y, exploiting the intrinsic concentration dependent optical properties of the Y-H system.9 Especially the progression of the boundaries separating the various stable hydride phases can easily be detected as discontinuities in the optical contrast.

The main purpose of this communication is to demonstrate that visualization of H diffusion is also possible for hydrogen in opaque transition-metal films. More specifically (i) we demonstrate the feasibility to use a thin layer of Y as an optical indicator to visualize the lateral H migration in thin films of vanadium, (ii) we show that the mobility of the phase boundaries in a composite film (e.g., V/Y) can be tuned through the sample/indicator thickness ratio, and (iii) we determine quantitatively the H-diffusion coefficient in a vanadium film by means of our optical indicator method.

The samples are prepared by means of e-gun evaporation in an ultrahigh vacuum system (background pressure <10−9 mbar). A typical sample consists of a V stripe of length L=10 mm, width b=1 mm, and thickness 25 nm <d<250 nm. Usually 11 stripes of various thickness d are deposited onto one, polished amorphous quartz substrate. The V stripes are covered with a thin layer of yttrium as an optical indicator to visualize the lateral H migration in vanadium away from the Pd-covered region can easily be monitored optically in the Y indicator layer as the various yttrium hydride phases formed at different hydrogen concentrations exhibit characteristic optical properties.8,11 For example, the front corresponding to the coexisting α and β phases is clearly identified as a discontinuous change in transmission and reflection.8 In Y, the phase boundary of the hcp α-phase is cα,max = 0.2 H/Y and that of the fcc β-phase is cβ,min = 1.9 H/Y, thus ΔcI =

![Diagram of the sample design.](Image)
diffusion is in the positive x direction. The reservoir-sample interface lies at \( x = 0 \) and \( c_S(x = 0) = c_{S0} \). The concentration \( c_S(x, t) \) is determined by the diffusion equation

\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right).
\]

(1)

Since (i) the enthalpy of hydrogen solution in the indicator (here Y) is much more negative than in the sample (here V) and (ii) the diffusion constant \( D \) in the sample (V) is orders of magnitude larger than in the indicator (Y), all the hydrogen flows via the sample into the indicator. This creates a diffusion front at \( x = x_f \) that is experimentally found to move as \( x_f^2 = Kt \). The H atoms crossing in the time interval \( \Delta t \), the cross section \( d_x \), at \( x_f \) are used (i) to move the front by \( \Delta x_f \) and (ii) to fill the overlying indicator up to a concentration of 1.9 H/Y. In this way \( c_f d_x \Delta x_f \) hydrogen atoms are accommodated in the sample and \( \Delta c_f d_x \Delta x_f \) in the indicator. As long as the indicator is still in the dilute YH\(_2\), \( \alpha \)-phase it takes up all the hydrogen from the underlying sample. There is essentially no difference in position between the position of the front in the indicator and the sharp drop of concentration in the sample at \( x_f \). Conservation of the number of particles leads to

\[
j_f d_x \Delta x = b (\Delta c_f d_x + c_f d_x) \Delta x_f,
\]

(2)

where \( j_f = -D_f (dc_f/dx) \big|_{x_f} \) is the flux of H atoms at the front through the sample. Assuming a concentration independent \( D \), the solution of Eq. (1) with \( c_S(0, t) = c_{S0} \) and the boundary condition Eq. (2) is

\[
c_S(x, t) = c_{S0} - \alpha \text{erf} \left( \frac{x}{2\sqrt{D}t} \right). \tag{3}
\]

As the concentration \( c_f \) at the front is given by

\[
c_f = c_S(x_f, t) = c_{S0} - \alpha \text{erf} (\sqrt{K/2\sqrt{D}}), \tag{4}
\]

we obtain from Eqs. (2) and (3)

\[
\frac{d_I}{d_S} = \frac{2 \alpha \sqrt{K}}{\Delta c_f \sqrt{\pi K e^{K/4D}}} + \frac{\alpha}{\Delta c_I} \text{erf} \left( \frac{\sqrt{K}}{2\sqrt{D}} \right) - c_{S0} \frac{\Delta c_I}{\Delta c_f}. \tag{5}
\]

In an experiment \( d_I/d_S \), \( \Delta c_f \), and \( K \) are known. The diffusion coefficient \( D \), the parameter \( \alpha \), and the equilibrium concentration \( c_{S0} \) can be extracted from measurements of \( K \) as a function of \( d_I/d_S \). The experimental data for two different sets of experiments (each of them for five values of \( d_I/d_S \)) are represented in Fig. 3 together with their respective fits.

We obtain a hydrogen-diffusion coefficient in vanadium \( D_V = 1.2 \times 10^{-5} \text{cm}^2/\text{s} \) and an equilibrium concentration \( c_{S0} = 0.62 \text{H/V} \) at 473 K and at \( p_{H2} = 1 \text{mbar} \). At \( T = 373 \text{K} \) and \( p_{H2} = 1 \text{bar} \) the measured values are \( D_V = 0.67 \times 10^{-5} \text{cm}^2/\text{s} \) and \( c_{S0} = 0.83 \text{H/V} \).

For a discussion of these results we assume first that the phase diagram of H in V films is the same as for bulk VH\(_2\). Then our results at \( T = 473 \text{ K} \) pertain to the \( \alpha\)-VH\(_2\) phase in which H occupies randomly tetrahedral sites in the bcc V lost lattice. Our results at \( T = 373 \text{ K} \), on the other hand, corre-
in the pressure range of $c_S$ concentration. Andersson et al. have studied by Andersson et al. a large miscibility gap. However, within experimental uncertainties between 450 and 500 K. In the case of our measurement, investigated here, is related to the tracer diffusion coefficient $D_t$ via $D/D_t=(c_S/k_B T)(\partial \mu/\partial c_S)$. Nuclear magnetic resonance (NMR) experiments on bulk vanadium show a monotonic decrease of $D_t$ with increasing hydrogen concentration $c_S$ from $D_t=2 \times 10^{-5}$ cm$^2$/s at $c_S=0.02$ H/V down to $D_t=2 \times 10^{-7}$ cm$^2$/s at $c_S=0.68$ H/V. The slope of the 473 K solubility isotherm at $c_S=0.62$ H/V yields $(c_S/k_BT)(\partial \mu/\partial c_S)\approx 3$, leading to a diffusion coefficient of $D=6 \times 10^{-5}$ cm$^2$/s, comparable with our value of $D=1.2 \times 10^{-5}$ cm$^2$/s. Again, a comparison between samples prepared by different techniques, leading to different grain sizes, stress states, impurities etc., hampers a direct comparison.

Let us now focus on the results at $T=373$ K and $p_{H_2} = 1$ bar. Even though the phase diagram for bulk V-H may deviate markedly from that for thin films and nanocrystalline samples, under the condition of 1 bar and 373 K we expect our V samples to be in the saturated $\beta_2$-phase. For bulk samples this phase boundary lies at 0.82 H/V and is essentially temperature independent between room temperature and 373 K. The H-rich $\gamma$-phase cannot be reached at 373 K without applying high pressures (ca. 50 bar), so we exclude the presence of this phase in our samples. Orimo et al. report a modification of the $\beta_2$-$\gamma$ phase boundary in the V-H system within nanometer-scale V grains. They conclude that the $\beta_2$-$\gamma$ phase boundary decreases from 0.82 H/V for 80-nm grains down to 0.67 H/V for 10-nm grains. By using NMR techniques, the same authors measured a hydrogen jump rate of $\nu_{300 K}=10^9$ s$^{-1}$ at 300 K in 80-nm-sized V grains with $c_S=0.82$ H/V. Using an activation energy of 240 meV, we obtain a jump rate $\nu_{373 K}=6 \times 10^8$ s$^{-1}$ at 373 K. Together with a jump length of 0.15 nm, the distance between two interstitial sites, this results in a tracer diffusion coefficient of $D_t=2.3 \times 10^{-7}$ cm$^2$/s. Compared with our measured $D=0.67 \times 10^{-5}$ cm$^2$/s this implies $D/D_t=(c_S/k_BT)(\partial \mu/\partial c_S)=29$. This value is consistent with the steepness of the 373 K solubility isotherm near the $\beta_2$-$\gamma$ phase boundary.

In conclusion, we have demonstrated that thin layers of YH$_{1}$ can be used as indicators to visualize hydrogen migration in opaque transition metals such as vanadium. In addition, our optical method allows measuring the equilibrium concentration in the material under investigation and its macroscopic diffusion coefficient. In principle, our technique is applicable to any material that can be coated with a switchable metal-hydride mirror material as long as (i) its H-diffusion coefficient is higher than the one of the indicator and (ii) its hydrogen affinity is low compared to the hydrogen affinity of the indicator. Furthermore, by varying the sample/indicator thickness ratio the effective mobility of the hydrogen front in the indicator layer can be tuned over a wide range. In principle, $D$ can be varied at room temperature by four orders of magnitude between the extreme values of $H$ in Y (typically $10^{-7}$ cm$^2$/s) and H in V (typically $10^{-5}$ cm$^2$/s). In a patterned thin film this opens the opportunity to locally vary the mobility of the front and to investigate hydrogen diffusion waves. Future investigations will include refractionlike and reflectionlike phenomena at interfaces separating areas of different effective diffusivities.

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