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Abstract. Neutron radiography is used to measure the hydrogen diffusion in metals. It is possible to work in a range of exposures where the optical density distribution on the radiographic film directly represents the hydrogen distribution in the sample. The method is essentially non-destructive and the hydrogen need not penetrate surfaces during the measurement. The diffusion coefficients of H in β-Ti, V, Nb and Ta in qualities as usually delivered were measured for temperatures between 50 to 110 °C. The results indicate that (i) the diffusion coefficient of H in β-Ti, Nb and Ta is not very sensitive to chemical composition and impurity content and (ii) the diffusion coefficient of H in V is much reduced by cold working without subsequent annealing. It is concluded that for most technical applications regarding the H transport properties it is not necessary to use extremely pure metals.

1. Introduction

There has been an increasing interest in the last few years in hydrogen in metals. On the one hand, hydrogen dissolved in metals provides the solid state physicist with a not too complicated model with which to study relations between the micro-structure and the properties of various materials. On the other hand, hydrogen in metals has technological relevance; examples being hydrogen embrittlement, problems of structural materials for possible fission reactors and hydrogen energy systems.

The present work deals with the application of neutron radiography to the study of the diffusion of hydrogen in metals. Neutron radiography has already been applied to the measurement of hydrogen diffusion in liquids (Chountas and Rauch 1968, Mannoussakis *et al* 1975). Neutron radiography allows us to obtain directly a photographic image of the hydrogen distribution in a sample. By evaluation of that image quantitative results can be obtained. With neutron radiography it is possible to observe and measure the bulk motion of hydrogen in metals with no direct observation of atomic processes as done for example by the quasi-elastic neutron scattering technique (Gissler 1972). The application of the neutron radiographic method to the investigation of hydrogen motion will be demonstrated in the present paper by measuring the bulk diffusion coefficient in some metals of technological importance.

2. Experimental

2.1. The neutron radiographic method

Disregarding multiple scattering thermal neutrons are attenuated by a sample according to the well known exponential relation

$$I = I_0 \exp\left(-Ld \sum_i \frac{\rho_i \sigma_i}{A_i}\right). \tag{1}$$

Here, I and I_0 are the neutron intensities with and without the sample, L is Avogadro's number, d is the thickness of the sample, ρ_i, σ_i and A_i are the density, the total microscopic cross section and the atomic weight of the ith constituent of the material investigated. The great advantage of neutron radiography is based on the property, that the cross section σ varies very irregularly from element to element and from isotope to isotope. So in particular, hydrogen has one of the highest total cross sections of all elements for thermal neutrons. Table 1 shows the cross sections of the materials investigated in the present work.

Table 1. Absorption (σ_a), scattering (σ_s) and total (σ_t) thermal neutron cross sections of elements relevant to this work (Mughabhab and Gardner 1973, Bacon 1975).

Cross sections (barn)	H	Al	Ti	V	Cr	Nb	Ta
σ_a	0·33	0·23	6·1	5·04	3·1	1·15	21·0
σ_s	81·5	1·55	4·4	5·1	4·1	6·6	6·2
σ_t	81·83	1·78	10·5	10·14	7·2	7·75	27·2

In neutron radiography the transmitted neutrons are recorded on a x ray film with a suitable converter foil in direct contact with it. The most widely used technique employs a 25 μm thick Gd foil on the back of the film. In order to obtain the hydrogen concentration from the optical density of the films a calibration procedure could be established in principle which uses a series of samples with known hydrogen content. In practice, such a procedure can be rather cumbersome because it requires a separate calibration procedure for every metal investigated.

Significantly, neutron radiography provides a possibility to work with good accuracy in a specific range of exposures, where such a calibration procedure is not needed. A useful feature of nearly all film converter combinations (Hawkesworth 1969, Berger 1965) is that their characteristic curve—which represents the optical density of the films as a function of the neutron exposure—exhibits a part where this density D is a logarithmic function of the exposure E

$$D = G \lg(E/E_0). \tag{2}$$

Here G is the 'gradient' of the film and E_0 is a 'threshold exposure' of the film. Therefore, the density difference for two different exposures with and without a sample in the beam is

$$D_2 - D_1 = G \lg(I/I_0) \tag{3}$$

where I is given by equation (1). Figure 1 shows two characteristic curves for the film converter combination used (Osray TA T4 film, 25 μm Gd foil, back technique).
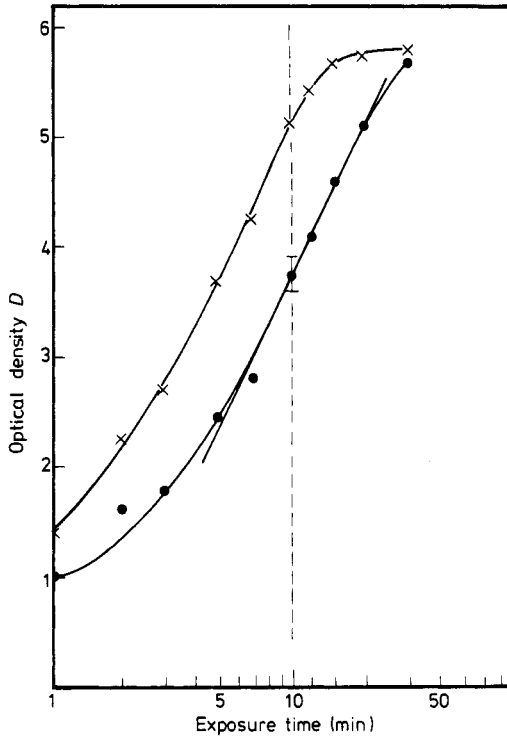
Figure 1. Characteristic curves of the film converter combination used: ×, without sample and ●, with Ta sample. The characteristic curve when a Ta sample is in the neutron beam is shown because Ta has the highest cross section of the investigated metals.

The straight part of the curves is shown explicitly. Writing now the sum in the exponent of equation (1) in the form

$$\sum_i \frac{\rho_i \sigma_i}{A_i} = \sum_j \frac{\rho_j \sigma_j}{A_j} + \frac{\rho_H \sigma_H}{A_H} \tag{4}$$

where the summation j is taken over all constituents except hydrogen we finally obtain the density difference ΔD_H due to the hydrogen content of the sample as

$$\Delta D_H = -0.4343\, GLd\rho_H \sigma_H / A_H. \tag{5}$$

This implies that when radiographing a sample which is homogeneous with respect to other constituents, the density distribution on the film is in a simple linear relation to the hydrogen distribution in the sample, i.e. neutron radiography provides a means to map differences in hydrogen concentrations.

A condition which has to be proved when equation (5) is applied concerns equation (1) which is only valid in the limit of negligible scattering. This problem arises because the high total cross section of hydrogen is mainly due to incoherent scattering. Therefore, the geometry has to be chosen so that the fraction of scattered neutrons which reach the converter foil—irrespective of whether single or multiple scattered ones—is negligibly small compared to the fraction of neutrons passing through the sample without being scattered. The influence of that effect can be reduced by

enlarging the distance between the sample and the converter. In the limit of an object small compared to the object-converter distance D this influence reduces as $1/D^2$.

Therefore, when one works within the limits where equation (5) is applicable, a densitometric scan of the film directly represents a hydrogen concentration profile of the sample because all quantities occurring in that equation are constant except the hydrogen density ρ_H. However, in some experiments one also wants to know the absolute hydrogen concentration besides the form of its distribution in the sample. In that case an estimate can be given by calculating the hydrogen concentration from the measured density using equation (5). The gradient G of the film can easily be determined from the characteristic curve, but the total cross section of the hydrogen is usually not known exactly for the particular experiment because the energy distribution of the neutrons in the beam is generally not known very accurately and because the cross section is a function of the type of binding of the hydrogen. In view of this latter point, calibrations with some other hydrogen containing substances can possibly lead to erroneous results but nevertheless a good estimate of the hydrogen concentration can be obtained.

2.2. Sample preparation and performance of the experiment

We investigated the metals β-Ti(13–11–3), V, Nb and Ta. All metals were in sheet form. Table 2 gives the suppliers of the metals, their sheet thickness and chemical composition. All metals were cold-rolled and (except V) annealed by the manufacturer. We did not perform any additional annealing or outgassing procedure because we wanted to provide the user of these metals with reliable data and to give an idea of the difference of the hydrogen transport properties of metals with commercial quality compared to pure metals with data published elsewhere.

From every metal strips were cut with the measures $65 \times 10 \, \text{mm}^2$. These strips were loaded electrolytically up to half their height with hydrogen, the unloaded half was covered with an adhesive tape during the loading procedure. The attained hydrogen concentrations were 12 at% (β-Ti), 11 at% (V), 14 at% (Nb) and 10 at% (Ta). The electrolytic bath used was dilute H_2SO_4 at room temperature. Several sheets of

Table 2. Data of the investigated metals.

| Metal	Supplier	Sheet thickness (mm)	Composition according to supplier, β-Ti actual, others typical (main constituents in at%, impurities in PPM)
β-Ti	Contimet Krefeld FRG	1·2	Ti 72·4, V 13·5, Cr 10·8, Al 3·0; impurities: Fe 1200, C 220, O 1300, N 280, H 105
V	Gesellschaft für Elektrometallurgie Nürnberg FRG	1	V > 99·7; impurities (max): Si 1500, C 150, N 200, H 5, O 200, Al 500, Fe 500
Nb	Metallwerke Plansee Reutte/Tirol, Austria	0·7	Nb + Ta > 99·91; impurities: Ta < 5000, Fe 500, Ti 50, C 100, O_2 500, H_2 10, N_2 100; distillation residue: 200
Ta	Metallwerke Plansee Reutte/Tirol, Austria	1	Ta + Nb > 99·93; impurities: Nb < 1000, Fe 100, Ti 50, Mo 300, W 300, C 30, O_2 50, H_2 10, N_2 50; distillation residue: 200
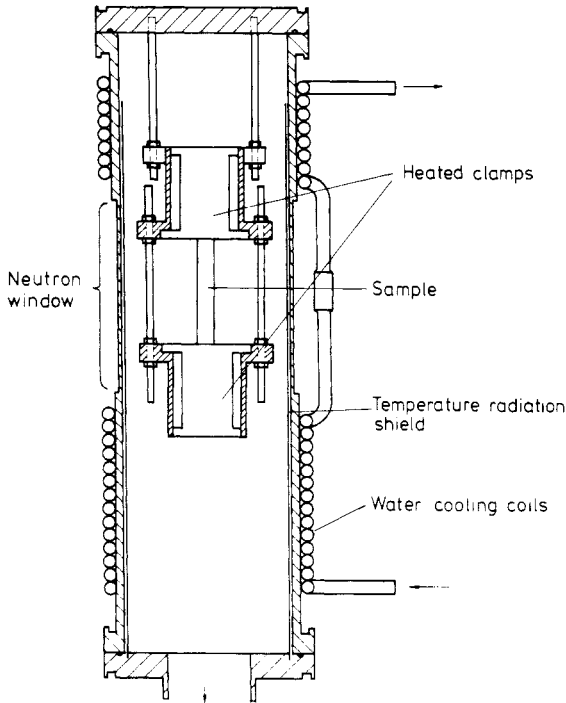
Figure 2. Schematic sketch of the furnace used for *in situ* radiographing the samples.

the same metal were loaded together under identical conditions and then sandwiched to give a sample of about 6 mm thickness to increase the radiographic contrast.

To measure the diffusion process at different temperatures, a furnace with walls penetrable for neutrons was used (figure 2). This enabled us to radiograph the samples without removing them from the furnace and thereby interrupting the diffusion process. The sample was mounted between two clamps which were heated by a standard resistance heating unit. The temperature at the point where the sample contacted the clamps was measured with thermocouples with the temperature being remotely controlled. The water cooled aluminium walls of the furnace were thinner in the region of the sample to give good neutron transmission. For thermal isolation the whole furnace was evacuated and, additionally, a gold-coated aluminium shield inside the furnace acted as a reflector of the thermal radiation. The clamps which held the sample were mounted at the upper flange assembly thus providing easy accessibility to exchange the samples which was done by pulling the whole upper flange assembly out of the furnace. The samples were mounted into that furnace immediately after the electrolytic loading process. The samples were then heated to the desired temperature (50–110 C) and neutron radiographs were taken repeatedly for several diffusion times. For every metal and every temperature at least four radiographs were taken, one of which was at the beginning of the diffusion process. The exposure time was 10 minutes in a thermal neutron flux $6 \times 10^5 \mathrm{cm}^{-2} \mathrm{s}^{-1}$. The neutron radiographs were then scanned with a microdensitometer with a slit aperture of $75 \mu\mathrm{m} \times 2500 \mu\mathrm{m}$ the long edge oriented parallel to the initial border between hydrogen containing parts of the samples and hydrogen free ones. The neutron radiographic contrast induced by the hydrogen content was $\Delta D \sim 0.3$.

3. Results

Figure 3 (plate) shows typical neutron radiographs of the hydrogen diffusion processes in β-Ti and Nb respectively. The smearing out of the optical contrast with increasing time easily can be observed. With regard to these radiographs it is already possible to make by visual inspection the statement, that the diffusion process in Nb is much slower than that in β-Ti. Also, the difference in sharpness of the edge on the radiographs taken at the beginning can be explained by that way.

The solution of the one-dimensional diffusion equation for a step function as initial distribution and a constant diffusion coefficient D employs the error function (see e.g. Crank 1956)

$$c(x, t) = \frac{c_0}{2}\left[1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]. \tag{6}$$
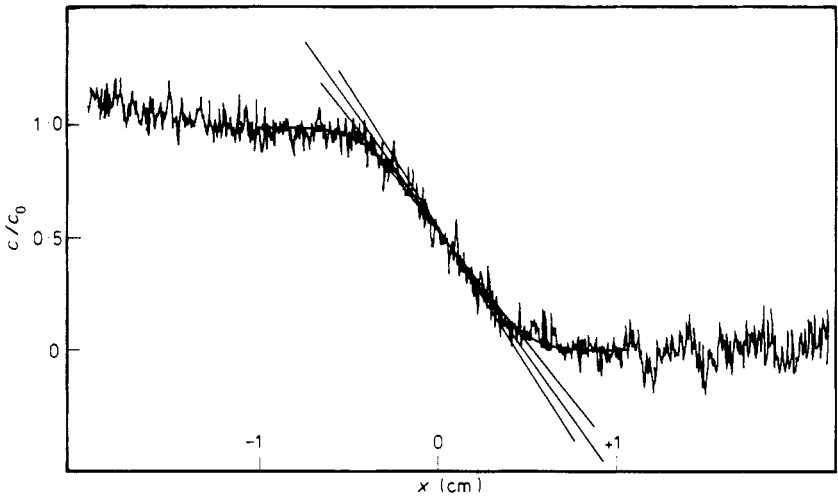

Figure 4. Typical densitometer scans shown together with the appropriate error function and three possibilities of the tangent $x = 0$ to estimate the measurement error.

Here c is the concentration, x is the distance from the initial boundary and t is the diffusion time. In figure 4 a typical densitometer scan of the neutron radiographs of these diffusion processes is shown together with the appropriate error function. Therefore, in principle the diffusion coefficient can be obtained by a fit of the error function to the experimental data. Another method which leads more rapidly to the diffusion coefficient makes use of the derivative of the distribution function at the point of inflection

$$\left(\frac{\partial c}{\partial x}\right)_{x = 0} = -\frac{c_0}{2\sqrt{\pi Dt}}. \tag{7}$$

In figure 4 three visually drawn tangents are shown to estimate the maximum error which can be introduced through a visual fit. The deviations between the diffusion coefficients calculated from these three tangents are $\pm 15\%$. The evaluation procedure described above was applied to every single diffusion profile, so the diffusion coefficients obtained for a certain temperature are the means of at least three measurements
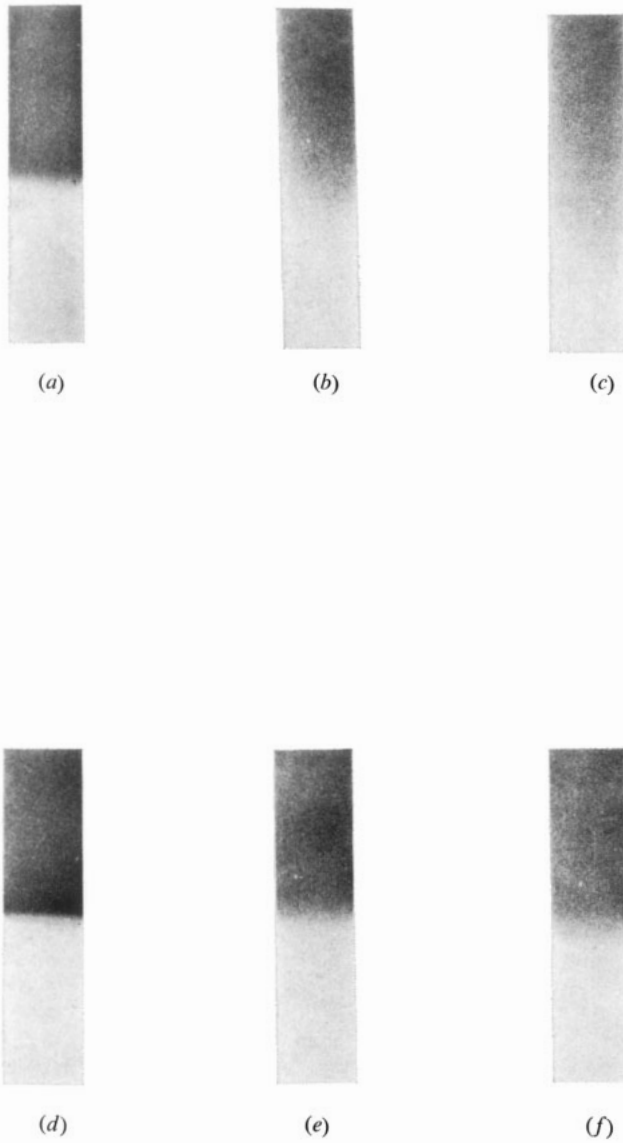
Figure 3. Neutron radiographs of hydrogen diffusion in metals. β-Ti measurements at 80°C, radiograph taken at (*a*), 0 h; (*b*), 18 h and (*c*), 48 h. Nb measurements at 75°C. radiographs taken at (*d*) 0 h; (*e*) 19 h and (*f*) 43 h.
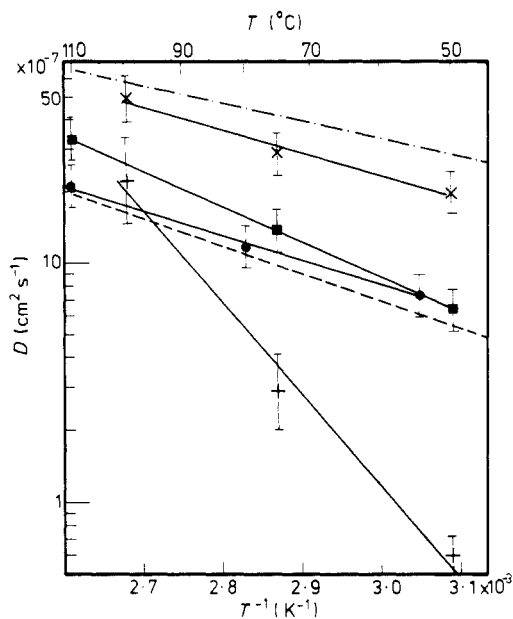
Figure 5. Diffusion coefficients of H in β-Ti ($\bullet$), V ($\blacksquare$), Nb ($+$) and Ta ($\times$). Also shown are the β-Ti results (---) of Holman *et al* (1965) and the Ta results (-·-·-) of Schaumann *et al* (1970)

at different diffusion times, the statistical error of these results was (the high-tempera-ture Nb measurements excepted) less than 3%. Therefore, we assume that the total error of the diffusion coefficient is less than $\pm 20\%$.

The diffusion coefficients of the four investigated metals are shown in figure 5. The results of β-Ti agree within experimental accuracy with those obtained by Holman *et al* (1965) for a very similar alloy. This demonstrates on the one hand the usefulness of the neutron radiographic method, on the other hand it can be concluded that the hydrogen diffusion property of at least that particular alloy is not very sensitive to small differences in chemical composition. In contrast, the diffu-sion coefficients of H in our V samples are more than one order of magnitude smaller than those in the pure metal (Schaumann *et al* 1970). This difference is evidently due to the fact that in our case the vanadium in its as delivered state was cold rolled but not annealed.

With regard to our results of the bulk H diffusion coefficient in Nb it has to be taken into account that in the concentration and temperature range of our measurements a miscibility gap exists in the phase diagram of the H–Nb system (Walter and Chandler 1965). In that region the α-phase coexists with the α' phase. According to Alefeld (1969 and 1975) the behaviour of H in Nb can be interpreted by phase transitions, the α phase corresponding to a lattice gas and the α' phase corresponding to a lattice liquid. Therefore measured bulk diffusion coefficients can show a marked deviation from the Arrhenius line, an effect which also was observed by Völkl (1972). For our sample of 14 at% H the α phase boundary should be reached at about 120 °C (Walter and Chandler 1965) and the Arrhenius-type behav-iour is expected to be attained at higher temperatures at which our results would come into the 10^{-5} cm^2 s^{-1} region in agreement with results obtained by other

authors for comparable hydrogen concentrations (Gissler *et al* 1970, Völkl 1972). Additionally, our low-temperature results are in the same order of magnitude as that one obtained by Alefeld *et al* (1972) for a hydrogen concentration of 9%. Furthermore we want to point out that some of our diffusion profiles of the H–Nb system obtained at 100 °C and 75 °C showed large deviations from the error function form. These deviations gave the distinct impression of two components diffusing with different velocities. Therefore, the interpretation of these diffusion profiles was not completely without ambiguity leading to larger errors of the diffusion coefficients as shown in figure 5. Furthermore in view of that discussion the possibility of fitting our data with a straight line is rather accidental and cannot be interpreted as aŋ Arrhenius line.

The agreement of our results for the H–Ta diffusion process with data obtained by Merisov *et al* (1966), Züchner and Wicke (1969) and Schaumann *et al* (1970) again is very good, the results of the last authors are included in figure 5. The difference between their results obtained with very pure (99·996%) and outgassed samples and ours evidently can be assigned to the fact, that we, in contrast, investigated the Ta in the as delivered state as stated above.

4. Concluding comments

We have demonstrated that neutron radiography is a feasible method to study the hydrogen motion in metals. When that method is used the hydrogen atoms need not pass the surface of the metal during diffusion. Neutron radiography provides a photographic image of the hydrogen distribution in a sample. The densitometric evaluation and the calculation of the diffusion coefficient is very straight forward and leads in a short time to results. From one single diffusion process at a given temperature many diffusion profiles can be obtained thus improving the accuracy of the method. A possible further improvement would concern the use of photographic films with smaller grain size thus reducing the instrumental noise and giving better spatial resolution. To overcome the then arising necessity of higher exposures a neutron beam of higher flux would be desirable.

The measured diffusion coefficients of β-Ti, Nb and Ta in as delivered quality indicate that the influence of impurities on the hydrogen transport properties is rather small. More severe is the effect of internal strains and stresses as our results obtained for an unannealed V sample show. Nevertheless all these differences are small when compared for example with the difference of the diffusion coefficients of H and O in Nb which in the temperature range of our investigations is as large as fifteen orders of magnitude. Therefore we conclude that for technical applications making use of the hydrogen transport properties of these metals the qualities usually delivered should be satisfactory provided the metals were annealed; further purification procedures would not be necessary.

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