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Physical and Corrosion-electrochemical Properties of the Niobium-Hydrogen System

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Electrochemical and physical aspects of the dissolution of hydrogen in niobium with an ideal or a real structure are discussed. The interactions of hydrogen with various crystal lattice defects and the changes in physico-mechanical characteristics of niobium caused by hydrogenation are analysed. Data on the kinetics and mechanism of non-equilibrium cathodic and anodic processes on hydrogenated samples of monocrystalline or polycrystalline niobium are examined, and the changes in chemical stability towards corrosive media resulting from saturation with hydrogen are discussed.
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I. INTRODUCTION

Niobium is one of the most corrosion-resistant metals. In recent years it has been used not only as an additive in the production of special alloy steels but also as a construction material. The rapid increase in the production and application of niobium has stimulated extensive studies of its corrosion-electrochemical properties in aggressive media, because the main areas of applications of this metal are in the chemical industry, in nuclear and hydrogen energetics, and in various new technologies such as microelectronics, apparatus construction, photoelectrochemistry, etc.

Niobium can readily occlude gases (H_2, N_2, O_2). Their absorption is accompanied by structural and phase changes in the metal. The gas most actively sorbed by niobium is hydrogen, and extensive studies of the effect of hydrogenation on the physico-mechanical characteristics and on the corrosion-electrochemical behaviour of niobium in corrosive media have recently been reported. The importance of this information is obvious, because the wide-ranging applications of niobium and its alloys have not so far been guided by an adequate understanding of the nature of the passive state of niobium and niobium alloys in hydrogenating media.

Published information on the corrosion-electrochemical behaviour of niobium containing dissolved hydrogen is scattered throughout a variety of papers reflecting the physical aspects of the problem, or discussing the corrosion resistance of niobium in aggressive media. Electrochemists and materials scientists are mainly interested in the time-scale of the chemical stability of niobium and its alloys in corrosive media under

conditions in which the metal is hydrogenated and its passivity may be impaired.

Both theoreticians and experimenters are interested in the formation of various phases in the Nb–H system, depending on the amount of hydrogen absorbed, and the very large volume of hydrogen which can be sorbed (up to a concentration corresponding to the composition NbH_3) suggests potential applications of niobium not only in nuclear energy but also as an occluder in hydrogen generators. This review examines the thermodynamic properties of the Nb–H system, problems associated with the dilatation of the niobium lattice caused by the penetration and diffusion of hydrogen, and the interaction of hydrogen with various defects of the metal lattice, as well as the final result of this interaction: the change in the physico-mechanical characteristics of niobium.

II. THERMODYNAMIC CHARACTERISTICS OF THE NIOBIUM–HYDROGEN SYSTEM

Niobium at room temperature absorbs a negligibly small amount of hydrogen from the gas phase.[1] The dissolution process begins only when the surface has been activated by high-temperature heat treatment (in the case of saturation from the gas phase) or by cathodic polarisation (if an electrochemical method of saturation is used). In the latter case the solubility of hydrogen in niobium at 293 K is sufficient to give an atomic ratio $\Phi_{H/Nb}$ as high as 0.68, the amount of hydrogen absorbed depending on the purity of the niobium.[2] In niobium of 98.5% purity the solubility (P_M) is 10 400 cm^3 H_2 per 100 g of metal (M), whereas in 94.8% Nb P_M = 5500 cm^3 per 100 g M, i.e. it is lower by about a factor of 2.

Structural characteristics of niobium hydrides.

Phase	Arrangement of metal atoms	Arrangement and coordination of hydrogen atoms	Stoichiometry and structure type	System, space group	Parameters of unit cell, A	z	Refs.
α (>440 K)	b.c.c.	Disordered, tetrahedral	—	Cubic, *Im3m*	$3.43<a<3.45$	2	[11,13]
ζ (212–232 K) *	b.c.r.	Ordered, tetrahedral	Nb_2H	Orthorhombic, *C222*	$a\approx b=4.9$; $c=3.47$	2	[14]
β *	f.c.r.	ditto	NbH	Orthorhombic, P_{nnn} or C_{ccm}	$a=4.85$; $b=4.92$; $c=3.47$ ($\Phi_{H/Nb}=1$)	4	[11,12, 15,16]
γ (<180 K)	b.c.c.	»	NbH	—	$a=3.44$	—	[11]
λ	—	Ordered	NbH ($\Phi_{H/Nb}\approx0.8$)	Cubic	—	—	[12]
ε	—	Ordered	Nb_3H_3	—	$a\approx b=9.8$; $c=3.47$	—	[15,17, 18]
δ	f.c.c.	Ordered, tetrahedral	NbH_2	Cubic, *Fm3m*	$a=4.55$	4	[19]

Symbols: b.c.c., body-centred cubic; b.c.r., body-centred rhombic; f.c.r., face-centred rhombic; f.c.c., face-centred cubic lattice; *z* is the number of atoms in the cell.
*For these phases the coordinates of the wave vector **k** are ($\frac{1}{2}$, $\frac{1}{2}$, 0).

The early workers[3–5] could not detect hydride phases corresponding to a definite stoichiometric ratio in hydrogen-containing niobium. However, a detailed phase diagram of the Nb–H system has now been assembled (Fig.1) by the application of X-ray, neutron, and electron diffraction methods.[6,7]

At room temperature an increase in the $\Phi_{H/Nb}$ ratio is accompanied by a gradual α → β transformation, followed by the formation of a (β + γ) phase. The phase diagram was constructed by using very pure niobium (99.99 at.%); the α and α′ phase are disordered solid solutions of hydrogen in a body-centred niobium cubic lattice, in which the hydrogen (5–6 at.%) in the α phase occupies tetrahedral positions. Increasing $\Phi_{H/Nb}$ results in the formation of a β phase which is an ordered interstitial solid solution of hydrogen in niobium. The α and β phases can coexist at 293 K up to $\Phi_{H/Nb}$ = 0.73.

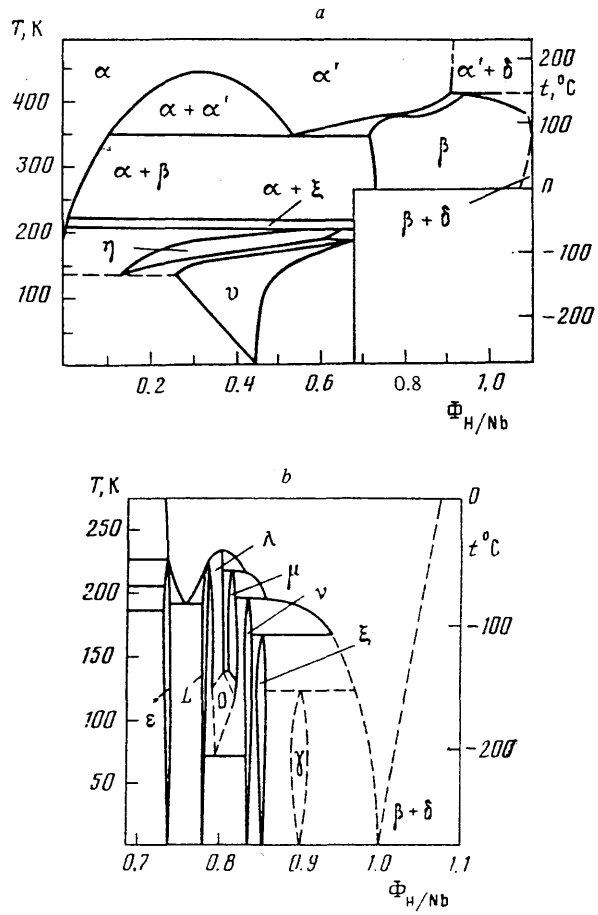


Figure 1. (*a*) Phase diagram of the Nb–H system; (*b*) low-temperature region of the phase diagram, for high concentrations of hydrogen in the niobium.[6,7,8–10] The broken lines define the regions for which no experimental data are available.

According to X-ray diffraction studies[11,12] the β phase has a face-centred rhombic lattice, and the α phase disappears at $\Phi_{H/Nb} > 0.73$. At $\Phi_{H/Nb} \leq 1.05$ only the β phase is observed (see Table), but at higher values of $\Phi_{H/Nb}$ a δ phase appears within the β phase, with a face-centred cubic lattice and corresponding to the compound NbH_2. The structural characteristics of the stoichiometric niobium hydrides are listed in the Table. Since a large proportion of the tetrahedral positions in the δ phase is occupied by hydrogen atoms, there is a high probability that the octahedral pores also may be occupied

under suitable conditions, but so far we have no experimental proof of the existence of the compound NbH_3. However, we should not forget that the kinetics of the transformations in the H–M systems can be strongly affected by exposure to X-rays.[20]

Electron microscope studies, both morphological and in transmission, have shown that both the β phase in the α structure and the δ phase in the β matrix consists of long needle-like formations resembling the β phase in titanium and its alloys. Of course, phase transformations giving rise to precipitates having a volume greater than that of the matrix produce hydrogen "embrittlement" in the main structure, accompanied by rearrangements in the fine structure.

Various experimental methods can be used in the construction of phase diagrams, and the shape of the curves separating the existence regions of the phases depends on the chosen method. Details of various regions of the Nb–H diagrams have recently been determined, both at low ($\Phi_{H/Nb} \leq 0.5$) and at high hydrogen contents ($\Phi_{H/Nb} = 1$). Thus, an unknown region of high hydrogen concentration between liquid helium temperatures and room temperature has recently been studied.[8] A combination of transmission electron microscopy and metallographic analysis has shown that a previously unreported[7] λ phase has an anisotropic cubic structure and can exist at $\Phi_{H/Nb} = 0.78–0.81$ and 207 K. At these very high hydrogen concentrations the precipitation of stoichiometric compounds of the Nb_4H_3 type (ε phase) is accompanied by the appearance of active H–H interactions and of lattice dilatation processes (discussed below). A detailed study of the phase diagram for $\Phi_{H/Nb} \leq 0.5$ has shown[3] that the coexistence region of the α′ and the β phase is wider than suggested by X-ray measurements of lattice constant.[7] It has been reported[10] that regions of existence of η and θ phases can be identified at $\Phi_{H/Nb} < 0.7$ and temperatures below 200 K; the ν, *L*, *o*, μ, γ, and ξ phases also proposed have not yet been adequately investigated but will probably be confirmed by various experimental methods (as was done for the α, β, and δ phases).

As was stated above, Nb–H phase diagrams constructed from different experimental data can be markedly different. Thus, according to the Horner and Wagner theory,[21] which describes the H–H interaction as the result of the elastic anisotropic distortion of the lattice produced by the interstitial hydrogen atoms, the maximum in the curve separating the α′ and the (α + α′) phases is at 470 K and $\Phi_{H/Nb} = 0.36$, whereas according to measurements of lattice constants by X-ray diffraction this maximum lies at 443 K and $\Phi_{H/Nb} = 0.3$. These discrepancies probably arise because the samples (of different geometry) used in the various measurements contain a range of native structural defects, and the structure-sensitive methods used by different workers have different responses to the different types of defect produced by hydrogenation.

We should stress the need to allow for the geometric shape of the sample and for the extent of deformation in studies of phase transitions in the hydrogen–niobium system. Thus, a study[22] of the α–α′ transformation by X-ray structural analysis showed that in Nb–H alloys the lattice constant and the shape of the (440) line (from which the extent of the transformation was assessed) are strongly dependent on the extent of deformation and on the geometric shape of the sample (disk, foil, or wire). This effect should, of course, be correlated with differences in the concentration profiles in samples of different geometry.

Our understanding of phase transitions in the niobium lattice has been improved by studies of structures containing added hetero-atoms (O, N) by neutron-spectroscopy and resonance methods. The interaction of hydrogen with atoms of the matrix can be determined by both attractive and repulsive forces, depending on the type of deformation produced by the impurity atom. If the additive causes compression of the lattice the repulsion is predominant, but in the opposite case the predominant effect is attraction. The interaction of the hydrogen atoms with the lattice atoms is treated as the sum of contributions from electronic, elastic, and screening interactions with the ionic core of the lattice. For niobium (a typical 4d metal[23]) we can use the following empirical rule: impurity atoms from positions to the left of niobium in the Periodic Table act as hydrogen traps, whereas other atoms do not.

III. HYDROGEN IN THE IDEAL NIOBIUM LATTICE

It follows from the above discussion that hydrogen can exist in different states in the niobium lattice, and give phases corresponding to definite stoichiometric ratios, depending on the concentration of hydrogen absorbed by the metal. The hydrogen can be present both as dissolved atoms, occupying tetrahedral positions in the niobium lattice, and as H^- ions for high values of $\Phi_{H/Nb}$ (when niobium hydrides are formed).

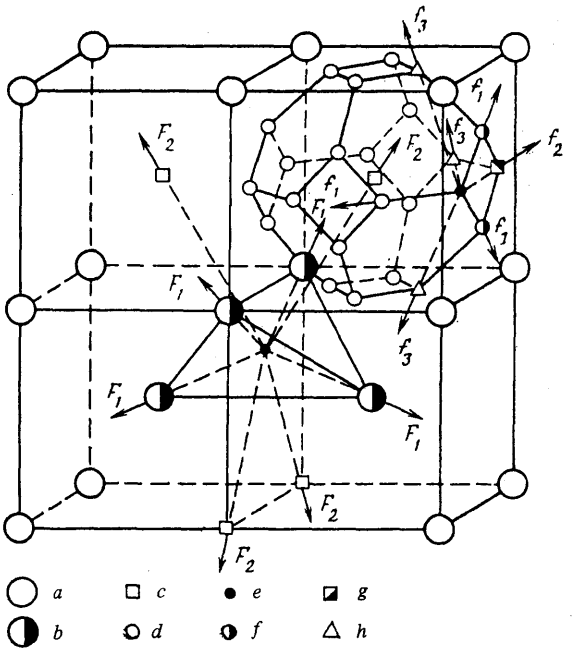


Figure 2. Radial Kanzaki forces (*F*) and H–H interaction forces (*f*) for stable positions of the hydrogen atoms in the tetrapores of the niobium lattice (the subscripts *1–3* denote the number of the coordination sphere).[28] In the diagram *a* are Nb atoms, *b* are Nb atoms of the first coordination sphere, *c* are Nb atoms of the second coordination sphere, *d* are tetrapores, *e* are H atoms, *f* are tetrapores of the first coordination sphere, *g* are tetrapores of the second coordination sphere, and *h* are tetrapores of the third coordination sphere.

Extensive experimental results obtained by neutron diffraction analysis and proton magnetic resonance methods show that tetrapores of three types (*x*, *y*, and *z* positions) are the stable sites for the introduction of hydrogen atoms. The radii of the hydrogen atom, of the tetrapores, and of the octapores

are, respectively, $r_H = 0.0460$ nm, $r_T = 0.0426$ nm, and $r_0 = 0.0225$ nm. Hence $\Delta r = r_H - r_T \cong 0.003$ nm, and therefore the stabilisation of a hydrogen atom in an interstitial site should produce an anisotropic deformation of the lattice.[24,25] This results in the partial filling of the octapores, with an occupancy of the tetrapores of ~1/6.[26] The probability of hydrogen atoms with parallel spins being accommodated in adjacent interstitials of the first and the second coordination spheres is believed to be low. At high levels of hydrogenation ($\Phi_{H/Nb} \leq 2$) the octahedral positions also can be partially filled with hydrogen atoms,[27] before the complete filling of the tetrapores.

According to Somenkov[26] when a tetrapore is filled with protium or deuterium (since the additional lattice distortion produced by the replacement of hydrogen by deuterium is small) the radial distribution of Kanzaki forces (the virtual forces acting on the neighbours of the inserted atom) takes the form shown in Fig.2. The Figure also shows the mutual disposition of the tetrapores in the Nb crystal lattice and the forces acting on the hydrogen atoms within these pores. A hydrogen atom of the centre of a tetrahedral pore produces an anisitropic deformation of the lattice. If another hydrogen atom is present in a neighbouring pore this deformation results in H–H interaction (or self-trapping), which is most marked under conditions of spin reorientation. If the hydrogen atom in adjacent interstitials have antiparallel spins the H–H interaction results in the formation of stable pairs. With a parallel arrangement of the spins the situation is less favourable to the formation of stable pairs. The stability of hydrogen in tetrapores has been experimentally demonstrated by neutron diffraction measurements.[26] The development of stable H–H interactions is accompanied by "swelling" of the hydrogenated crystal. Without allowing for anisotropic lattice deformation we can evaluate the relative change in volume $\Delta\nu/\Omega$ (where ν is the volume of the unit cell and Ω is the atomic volume) per unit concentration of hydrogen, of deuterium, or of tritium (c) as $\Delta\nu/\Omega = 0.174 \pm 0.005$ for low c and $\Delta\nu/\Omega = 0.14 \pm 0.08$ for high c.

The filling of the d level by the 1s electrons of the hydrogen strengthens the M–M bond, and this should affect the mechanical characteristics of the niobium crystal in the hydrogenated state (plasticity, shock viscosity, strength, etc.). These characteristics are strongly dependent on the local dilatation of the Nb lattice, caused by the formation of hydride in limited volumes,[29] which stimulates the rearrangement of submicrostructures and thus affects the corrosion-electrochemical properties of niobium. The formation of clusters involving hydrogen is determined by the diffusional transport of the hydrogen in the lattice.

The diffusion problem can be discussed either in terms of the classical "jump" mechanism, according to which the diffusion act requires an amount of energy sufficient for a hydrogen atom in a tetrapore to surmount the diffusion barrier, or (in quantum-mechanical language) by identifying the interstitial atom with a small polaron, whose displacement is non-activated (tunnelling, or under-barrier transition).

According to Stoneham[30] there are two major differences between the quantum and the classical theory of diffusion of hydrogen in metals. The first is the quantisation of the energy levels, the second is the existence of a zero point relative to which the lattice distortions can be determined in the neighbourhood of a light impurity atom. In the jump mechanism for the displacement of hydrogen in the metal the probability of a jump is described by a simple equation of the Arrhenius type:

$$\Gamma \sim J^2 \cdot \exp(-E_a/k_B T) \qquad (1)$$

where J is a tunnelling matrix element, given by

$$J = \frac{8\hbar^2}{2md^2}\left(\frac{2md^2}{\hbar^2}\Delta\psi\right)^{3/4} \cdot \exp\left[-\frac{2}{\pi}\left(\frac{2md^2}{\hbar^2}\Delta\psi\right)^{1/2}\right] \qquad (2)$$

and m is the number of the metal atom, d is the distance between the potential minima (the positions of the hydrogen atom in a stable state), and $\Delta\psi$ is the depth of the potential well.

Calculations[30] of the tunnelling matrix elements by formula (2) show that for niobium J is determined essentially by d and amounts to 1.45 MeV. The exponential factor in Eqn.(2) corresponds to a configuration in which the adjacent positions occupied by a proton before and after the diffusion act are equivalent.

The theory of small polarons treats a proton in a potential well before the diffusion act as having a lower energy than the adjacent interstitials. At the completion of the diffusion act the opposite situation exists. In the classical diffusion theory the quantity E_a corresponds to the relaxation energy at the instant when the proton is half-way to the second interstitial. Recent developments in the theory of small polarons have shown the need to allow for the dependence of J on the normal coordinates of the vectors for the displacement of the Nb atoms from their equilibrium positions. In this case, since in a b.c.c. metal lattice the hydrogen atoms are accommodated in tetrahedral interstitials, according to Flinn and Stoneham[30] the parameter Γ also depends on E_S (the energy needed to create a lattice configuration with normal coordinates large enough to give $J = J_{lim} = \text{const}$):

$$\Gamma = \frac{J_{lim}^2}{4\hbar\,(E_a E_s)^{1/4}} \cdot \exp[-(E_a + E_s)/k_B T] \qquad (3)$$

Thus the localised proton moving through the lattice by a thermally activated process to a large extent "determines" the barrier which it must overcome. The diffusion problem is mor complicated when the adjacent interstitial is occupied by a proton or by some other light impurity element. In this case the H–H interaction results in a more substantial deformation of the neighbouring interstitial, and the diffusion process is facilitated for the pair of hydrogen atoms. Of course, in an ideal crystal the diffusional displacement of hydrogen is anisotropic and occurs preferentially along certain crystallographic directions. Surmounting saddle-points in the lattice must be discussed with allowance for the interaction between migrating particles even when the proton is identified with a small polaron. At low concentrations of hydrogen in niobium ($c_H \leq 0.06$ at.%) the parameter E_a is linearly dependent on c_H. According to recent work,[31] and in contrast to earlier reports,[30] the average probability of a jump by a hydrogen atom in a niobium crystal for $c_H \leq 0.06$ at.% is

$$\Gamma = \omega \cdot \exp\{-[(E^b - E^a)/4 + e_0]^2/e_0 k_B T - B^2/k_B T\}/B \qquad (4)$$

where w is the vibration frequency of the hydrogen atom in the pore, and the quantities $(E^b - E^a)$, e_0, and B allow for the energy of the interaction between the diffusing hydrogen atoms.

It follows from (4) that the jump probability of a hydrogen atom in a niobium crystal, which depends on the activation energy for diffusion, is related to the vibration frequency of the hydrogen atoms in the pores, and therefore also to the mass of the hydrogen isotope. The strong dependence of the diffusion of hydrogen in metals on the mass of the isotope and on the type of crystal lattice was stressed in a recent interview.[32] It was pointed out that in a b.c.c. metal the diffusion parameter E_a is smaller for protium than for deuterium, whereas the opposite is true in metals with a f.c.c. lattice. The activation energy for the diffusion of protium in tantalum and in niobium suddently decreases at $T < 250$ K, but it remains constant for deuterium and tritium. This shows that the quantum effects are more substantial in b.c.c. than in f.c.c. metals. On lowering the temperature stronger effects are observed.

It was reported[28] that E_a for the diffusion of hydrogen isotopes in the b.c.c. niobium lattice at 133–373 K increases with the mass of the isotope, as also found by other workers.[32] However, it was also noted[28] that in the niobium samples the pre-exponential factor in the Arrhenius expression (1) is almost independent of the mass of the isotope. In that work[28] the diffusion process was discussed in terms of the Gorskii effect, for which the stress relaxation force Δ_E (allowing for the motion of the isotopes in a field of elastic stresses) is given by the Curie–Weiss expression

$$\Delta_E = A\frac{c_H P^2}{T - T_s} \quad , \qquad (5)$$

where A is a constant depending on the elastic properties of the sample; T_S is the concentration-dependent spinodal temperature, which can be expressed as $T_S = uc_H/k_B$ for small concentrations of hydrogen in the metal (where u is the interaction energy); $3P$ is the dipole moment of the elastic deformation tensor (due to the presence of hydrogen), with $P_{ij} = \sum_m F_i^m x_i^m$ (F_i^m are the virtual Kanzaki forces acting on each atom m at a distance x_i^m from the defect site).

Therefore, as was stated above, it is essential to allow for the anisotropic dilatation of the lattice and for the change in lattice parameter a caused by the hydrogenation, which can be expressed as

$$\Delta a/a = (2c_H/a^3)P(S_{11} + 2S_{12}) \quad , \qquad (6)$$

where S_{11} and S_{12} are the elastic coefficients.

An analysis of experimental data for the niobium–hydrogen system has shown[12] that $\Delta a/a$ can be found by assuming a linear dependence of a on the concentration c_H:

$$\Delta a/a = (4.72 \pm 0.25) \cdot 10^{-4} c_H \quad , \qquad (7)$$

(where c_H is in at.%). By using (7), which is much simpler than (6) but does not allow for the anisotropic deformation of the lattice produced by hydrogenation, the concentration of hydrogen dissolved in the niobium can be determined with acceptable precision. From the results of various workers, reviewed in Ref.29, linear dependences of $\Delta a/a$ and $\Delta V/V$ (where V is the macroscopic volume of the sample) on the concentration of hydrogen in niobium are observed up to $\Phi_{H/Nb} = 1$. At attempt was made to explain these results in terms of the elastic interactions between hydrogen and niobium atoms by identifying the $\alpha \rightarrow \alpha'$ transition[33] with a gas → liquid transition.

It has also been reported[28] that at low concentrations of the hydrogen isotopes in niobium ($\Phi_{H/Nb} \cong 0.1$) the parameter E_a increases with the mass of the isotope (from hydrogen to tritium) from 0.068 to 0.133 eV, while the diffusion coefficient D_H is almost independent of the mass of the isotope.

IV. INTERACTION OF HYDROGEN WITH DEFECTS IN THE NIOBIUM CRYSTAL LATTICE

We have pointed out above the H–H pair interactions affect the diffusion of hydrogen. The hydrogen trapping phenomenon is found not only in interstitials but also in defects at higher dimensionality (vacancies and dislocations, single or in groups, grain boundaries, microscopic inclusions, and pores). The surface of the sample can also be treated as an energy trap. Let us examine the interaction of hydrogen and niobium with crystal lattice fectes of various dimensionalities.

1. Zero-dimensional Defects

The trapping of hydrogen by vacancies and vacancy clusters, by interstitial impurities (O, N), and by substitutional impurities (W, Mo, V, etc.) is of interest from the theoretical as well as from the practical standpoint. The latter impurities, being getter elements, have a substantial influence on the functional properties of Nb, especially those of technological importance (plasticity, shock viscosity, refractoriness, and corrosion resistance).

The hydrogen–vacancy interaction and the formation of vacancy–interstitial (hydrogen atom) pairs are usually treated as separate aspects in published papers. Hydrogen taken up by a single vacancy stabilises it and suffers a loss in diffusional mobility. However, it is possible for several hydrogen atoms to be adsorbed at a single vacancy, and this produces an anisotropic deformation of the lattice which results in an increase in the diffusional mobility of the vacancy–interstitial hydrogen atom pairs in some crystallographic directions. At high values of c_H the vacancy is transferred from one hydrogen atom to the next by a kind of "relay" mechanism.

Allowance for the change in mobility of the vacancy–interstitial hydrogen atom pair is essential at temperatures close to the melting point. "Anomalous superplasticity" has been observed experimentally in iron at high temperatures.[34] In the hydride-forming 4*d* metals, which include niobium, an increased concentration of hydrogen at the grain boundaries (i.e. at the sites where point defects are annihilated) may explain the change in mobility of these boundaries at relatively high temperatures. In materials previously deformed by large amounts (>90%) annealing after hydrogenation can yield larger-grained or even monocrystalline structures.

A study[35] of the low-temperature desorption of hydrogen from niobium has shown that at $T < 300$ K the formation of vacancy–hydrogen complexes is energetically favourable only for c_H values above the threshold of $\Phi_{H/Nb} > 2$. Further addition of hydrogen results in the merging of hydrogen–vacancy complexes into bubbles, detectable as low-temperature blistering (localised breakdown of the near-surface layer of metal).

Hydrogen can assist the combination of divacancies into vacancy clusters. The most stable clusters were found[31] to contain between three and six vacancies. Under these conditions we can expect the formation of gaseous hydrogen and pores of vacancies. However, because of the difficulty of producing vacnacies in b.c.c. metals very few experimental observations of this phenomenon have been reported, though one report[7] of the formation of screw dislocations near clusters of vacancies filled with hydrogen, detected by transmission electron microscopy, is noteworthy. The effects caused by the interaction of hydrogen in niobium with oxygen and nitrogen impurity atoms have been studied much more extensively.[37]

Nitrogen and oxygen atoms have relatively low mobilities in the niobium lattice at low temperatures, and therefore the capture of hydrogen atoms by nitrogen and oxygen atoms produces pairs with well defined configurations. Under conditions in which the interstitial oxygen atoms occupy octahedral positions the O–H pair can have a trigonal symmetry, i.e. be oriented in the <111> direction. The elastic interaction energy between an interstitial impurity accommodated in an octahedral position and a proton in an adjacent tetrapore has been calculated.[38] In this case the elastic energy is described by the expression

$$E = -F_0 Z F_\tau - \Delta E_\tau + \Delta E_0 \quad ,$$

where F_0 and F_T are the Kanzaki forces for interstial impurities in an octapore and a tetrapore respectively, Z is the harmonic lattice function in the near-surface layer of the pure

metal, ΔE_S is the energy of the H–H bond, and ΔE_0 is the binding energy of the proton on the zeroth energy level.

Experimental studies,[39,40] mainly by elastic relaxation methods in the frequency range 30–170 MHz, have shown that the hydrogen atom can occupy tetrahedral positions when pairs with a <100> orientation are formed preferentially. This suggests that the hydrogen atoms are not localised in the tetrapores but are uniformly distributed in ring-like structures consisting of four tetrapores and four triangular sites (0, 3/8, 3/8) and surrounding an octapore not containing an oxygen atom. In this case the motion of hydrogen in the Nb lattice is accurately described by the Flinn–Stoneham theory [see Eqn.(3)]. It has been reported[32] that nitrogen atoms in niobium lower the diffusion coefficient of hydrogen, and at $T < 5$ K the local diffusion of hydrogen trapped by nitrogen atoms takes place by under-barrier crossing (tunnelling): under these conditions the hydrogen atom migrates through 16 adjacent tetrapores of the b.c.c. niobium lattice. The nitrogen atoms were shown[41] to be concentrated in the octahedral interstitials of the Nb crystal lattice by the proton channelling method, using the $^{15}N(p, \alpha\gamma)^{12}C$ nuclear reaction.

Thus the diffusional transport of hydrogen along the tetrapores takes place round an octapore occupied by a heteroatom (O or N). Trapping states created by the interstitial atoms must lower the mobility of hydrogen in Nb.

It has been shown[42] that the decrease in mobility of H (or D) in niobium containing up to 1 at.% of nigrogen is most marked at low temperatures (<200 K). The effective diffusion coefficient of hydrogen depends on the concentration of interstitial sites in Nb occupied by impurity atoms:

$$D_H^{eff} = D_H(\partial c_H^f/\partial c_H) \quad , \qquad (8)$$

where c_H^f is the concentration of free hydrogen in the niobium. According to results obtained by an electrochemical method[43] the D_H^{eff} value in interstial alloys with $c_H \geq 0.03$ wt.% is $(1.80–3.90) \times 10^{-8}$ cm^2 s^{-1}.

It was recently confirmed[44,45] that at low temperatures (0.04–2 K) the trapping of interstial H and D atoms by oxygen impurities in niobium takes place by tunnelling. By measuring the temperature dependence of the specific heat experimental values of the tunnelling matrix elements were calculated by the Flinn–Stoneham theory, and no difference was detected between H and D interstitial atoms for oxygen concentrations ≤2 at.% in the niobium.

The situation in which oxygen is concentrated in the near-surface layer of niobium forming stoichiometric or non-stoichiometric Nb_xO_y compounds is of great practical interest. Extensive information is available on the structure and properties of these oxides. The substantial change in the concentration of hydrogen obtained by saturating niobium foils covered with niobium pentoxide Nb_2O_5 is due to the depletion of hydrogen in the surface layer.[46] These results were obtained by the $^1H(^{15}N, \alpha\gamma)^{12}C$ nuclear reaction, but a calculation of the thickness of the hydrogen-containing layers by an X-ray method gave almost the same result.

The effect of substitutional impurities (V, Ta, Mo) at low concentrations on the solubility of hydrogen in niobium has been studied.[46–50] Substitutional impurities are usually introduced in order to improve the mechanical properties and the inertness of niobium. Thus it was shown[49] that the solubility of hydrogen in Nb is raised by Ta, Mo, and (specially) V impurities. This effect is due to the energetically favourable interaction of H with the substitutional impurity atoms, which increases as the atomic radius of the alloying element is decreased with respect to the Nb lattice parameters (since the H atom decreases the lattice deformation produced by the alloying atom).

The bond energy of the hydrogen in tetrahedral positions round a V atom had been estimated[48] to be $E_{V-H} = 0.09 \pm 0.05$ eV, i.e. close to the bond energy in the complex between hydrogen and an interstitial impurity ($E_{H-O} = 0.09$ eV).[37] However, it was later shown[46] that the energy of the V–H bond has a much lower value (0.04 eV), and that trapping of hydrogen atoms on vanadium impurities in niobium is not normally observed between 2 and 293 K.[50] The probability of self-trapping of hydrogen and deuterium atoms and of μ^+ mesons in Nb crystals containing the substitutional impurities Ti, Cr, and V has been calculated.[51]

Recent experiments with Nb crystals containing substitutional Cr and Ti impurities[52,53] are inconsistent with the theoretical expectation of trapping of the hydrogen atoms mainly as a result of the deformation fields created by the impurities. A more general method, used in Ref.51, includes constructing the potential energy operator for the hydrogen in a suitably averaged crystal field, calculating the zero displacement of the hydrogen by an appropriate three-dimensional form of the Schrödinger equation, and finally evaluating the lattice distortions produced by the insertion of hydrogen (using a set of Green's functions as in calculations for static problems). This method was applied to the self-trapping of hydrogen, deuterium, and μ^+ mesons in Nb crystals containing Ti, Cr, and V substitutional impurities. Comparing the results with experimental data obtained by inelastic neutron scattering showed a generally good agreement: the few discrepancies were attributed to the simplifcations introduced in the calculation.

Of course, a much greater increase in the solubility of hydrogen can be expected in the presence of substitutional impurities from Groups V and VI, such as S, Se, Te, Bi, and Cr. In this case the increase in solubility results not only from the elastic distortions of the Nb lattice but also from the high energy of the bond between the hydrogen atoms and the elements of Groups V and VI.

2. Line Defects

The interaction between hydrogen and dislocations is very important in niobium, because it has a fundamental influence on the mechanical characteristics of the material. Extensive studies of the hydrogen–dislocation interactions have been reported: the most interesting result for b.c.c. metals is the non-conservative motion of the dislocations and the absence of a limited set of slip directions.

Phenomenological discussions of hydrogen–dislocation interactions are usually based on expression of the type of (1); the formation of a Cottrell atmosphere (the atmosphere of impurity hydrogen atoms surrounding the dislocation) can be described by the expression

$$c_H = c_H^0 \cdot \exp(\sigma_H V_H/RT) \quad , \qquad (9)$$

where c_H^0 is the equilibrium concentration of hydrogen in the lattice, v_H is the partial molar volume of hydrogen in the metal, and σ_H is the hydrostatic pressure of hydrogen. Attempts to allow for the dislocation core by the linear theory of elasticity[54] yielded a more complicated form of Eqn.(9):

$$c_H = \pi r_0^2 l c_H^0 \cdot \cosh(\sigma_H V_H/RT) \cdot \exp(\sigma_H' V_H/RT) \quad , \qquad (10)$$

where σ_H' is the additional pressure on the dislocation core resulting from the chemical hydrogen–dislocation interaction, l is the length of the dislocation, and r_0 is the radius of the dislocation core (~0.18 nm).

For large c_H^0 Eqns.(9) and (10) should be replaced by Fermi–Diract distribution expressions.[55] In the quantum-mechanical approximation Eqn.(10) contains additional terms

for the anisotropic nature of the hydrogen–dislocation interaction; Eqn.(10) should also contain terms allowing for the virtual forces (Kanzaki forces).

The hydrogen–dislocation interaction not only suppresses the mobility of the dislocations but it also affects their concentration, especially near the grain boundaries in a polycrystal. Thus it has been shown[56] that in the electrolytic hydrogenation of polycrystalline niobium the dislocation density ρ increases from 6×10^{11} to 1.3×10^{14} m^{-2} as c_H increases. This increase is attributed[56] to H–H interactions and to the precipitation of a hydride phase at the niobium grain boundaries, which activates a source of dislocations within the grain. A hydride phase can also be formed (at high P_H) directly within the grain, as a result of the inclusion of dissolved hydrogen atoms in clusters and local precipitation of hydride. Hydride formation takes place[57] as a cooperative rearrangement of the crystal lattice in small regions of supersaturated solutions of hydrogen in metals.

The most convincing evidence of hydrogen–dislocation interactions was obtained in studies of the relaxation properties of hydrogenated metals, in which the rearrangement of dislocation structures through reversible mechanical interactions is determined by impurities precipitated at dislocations. Thus a study of the stripping of dislocations from obstacles[58] in very pure polycrystalline niobium at 5–300 K by the internal friction method has shown that at $T < 70$ K the presence of hydrogen atoms leads to the pinning of dislocations. Similar results were obtained[59] at $T < 100$ K for high-purity niobium with a very low concentration of hydrogen (<10^{-6} at.%). The stripping of the dislocations from the anchoring points produces internal friction peaks. The dependence of the vibration frequency of the sample (f) on E_a and on the applied load (σ) is given by the expression

$$f = \nu_0 \cdot \exp\left(-\frac{E_a - \sigma V_a}{k_B T}\right) , \qquad (11)$$

where V_a is the activation volume, $\sigma = G\varepsilon_{max}$, G is the normal elastic modulus, ν_0 is the vibration frequency of the dislocations, and ε_{max} is the maximum deformation of the sample. It follows from (11) that decreasing V_a and G produces obstacles to the motion of the dislocations in a hydrogenated crystal. Obviously, this situation will be found in samples supersaturated with hydrogen.

The most detailed studies of the relaxation properties of hydrogenated niobium over a wide temperature range are described in Refs.60 and 61. Two peaks are found on the temperature dependence of the internal friction (Q^{-1}): the first (the α peak) at 123–143 K, and the second (the γ peak) at 263–268 K. In the absence of dissolved hydrogen the magnitude and position of these peaks depend on the extent of deformation of the niobium.[62] Increasing the vibration frequency of the hydrogenated niobium samples (f) from 0.49 to 3.4 Hz results in a degenerate γ peak, while the height of the α peak stays constant. On the other hand the height of the α peak is strongly influenced by the intensity of the preliminary deformation ε, and the signal is highest in the case of an annealed sample. The decrease in height of the peak with increase in f is attributed to hydrogen–dislocation interactions, and to the easier detachment of dislocations from their hydrogen atmosphere at higher frequencies. Allowance for the change in permeability of the dislocation stoppers as a result of hydrogenation is essential in the analysis of dislocation motions. Low-angle boundaries (consisting of dislocation walls) usually behave as strong barriers to the motion of dislocations. However, barriers such as grain boundaries, microscopic inclusions, etc. have an even greater effect.

3. Plane Defects

The changes in physical characteristics produced by the hydrogenation of niobium bicrystal samples are very fully characterised experimentally. It has been shown[63] that an iron bicrystal can be split into individual single crystals by hydrogenation under an applied stress. Large niobium bicrystals can be prepared by electron-beam zone melting,[64] with any required misorientation (δ); the dislocation density ρ in the bicrystal is higher than in a monocrystal grown under the same conditions (the ρ value was determined by measuring electrical resistance at room temperature and at liquid helium temperature).

When determining the rate of corrosion (K) along the boundary of a niobium bicrystal we must allow not only for δ but also for the crystallographic orientation $\{hkl\}$ of the contacting planes of the individual crystals, since the K value for a given plane depends on the $\langle hkl \rangle$ direction. Thus it has been shown[16] that for a $[011]/\langle 0\bar{1}1 \rangle$ boundary with $\delta = 16°$ the parameter K along the grain boundary and the extent of corrosion (d_K) go through a maximum; however, the resulting concentration profile is asymmetric because of the difference between the K values for different crystal planes. The dependences of δ on d_K are linear only for $\delta \leq 20°$. Beyond this point non-linearity is observed, and a minimum appears on the plot of d_K against δ for $\delta = 28°$, probably due to a change in the structure of the grain boundary with increasing δ. Whereas the number of coincident sites decreases regularly with increasing δ for small misorientations, when $\delta \geq 20°$ this number can fall away steeply after an initial increase.

Point defects can easily interact with ground boundaries, and therefore very pure bicrystals must be used in studies of the effect of hydrogen. The accumulation of large atoms of the p and sp elements at the grain boundary can greatly distort the structure of the boundary and affect its adsorption properties towards hydrogen. The diffusional mobility of hydrogen moving in the bulk of the grain or along the grain boundary has been calculated.[66] The diffusion coefficient D_H determined electrochemically for grain-boundary diffusion is usually two orders of magnitude greater than for the bulk of the grain.

4. The Surface

The most important defect of a solid is its surface. We have already mentioned the influence of surface oxidation on the absorption of hydrogen by niobium samples. The surface acts as a kind of filter which transmits the adsorbed hydrogen atoms. Therefore even slight contamination of the surface by foreign atoms can seriously alter the energy balance of the adsorption and of the subsequent penetration of the hydrogen into the metal. The largest effects are produced by surface oxygen, or (in the case of electrochemical processes) by water molecules adsorbed by their oxygen atom. A study by electron-stimulated desorption[65] has shown that oxygen adsorbed on the (110) and (100) niobium surfaces can be desorbed by H^+ ions. The ability of H^+ to desorb oxygen by the electrochemical reaction $H^+ + MO + \bar{e} \rightarrow 2M + OH$ depends on the crystallographic indices of the plane: the rate of desorption is lower on the less densely packed (111) plane.

The most widely used method of protecting the surface of the metal to be hydrogenated from oxidation is to deposit a layer of a noble metal (for example, palladium). This is often done in studies of the hydrogen permeability of membranes. However, we must allow for the change in the electronic structure of both metals resulting from the formation

of the Pd/Nb contact.[67] A large decrease in the density of *d* states of Nb at the Fermi level (E_F) after the adsorption of palladium was noted in a study of the (110) surface of the Pd/Nb contact. A decrease in the density of *d* states should lower the solubility of hydrogen in a transition metal, since the absorption of hydrogen is accompanied by interaction of the hydrogen *s* electron with the *d* band of the metal.

The hydrogen can exist in two types of bound state on the crystal surface (in other words, the energy level of the surface has two minima). In the case of one-centre adsorption on the first layer of atoms (*r*-type adsorption) the bond between H_{ads} and the surface is weaker. Hydrogen in the *r* form can diffuse along the surface, and it can form planar adsorbed structures with various periodicities on the billiard-ball packed (110) niobium surface. Hydrogen in the *s* state (in the second layer of surface atoms) is more strongly bound. In this case the less closely packed {111} surfaces can more readily form hydrogen structures in the *s* state. The rate at which an adsorbed hydrogen atom is transferred into the *s* state depends on the pressure of hydrogen on the metal surface. For monocrystalline samples the rate of crossing of the interfacial boundary by adsorbed hydrogen atoms is strongly dependent on (*hkl*), and the hydrogenation kinetics are determined by the combined processes at the surface and in the bulk of the niobium lattice. The contribution of the surface processes on the (110) niobium surface was found[68] to be predominant.

When the Nb surface is covered with oxygen the desorption of oxygen by hydrogenation should be easiest on the close-packed (110) surface and least effective on the (111) face. On the clean surfaces which can be produced by lengthy desorption treatment during hydrogenation the spin–spin interaction between the adsorbed hydrogen atoms cannot be ignored. The recombination and desorption of the hydrogen atoms from the surface take place most readily in the case of antiparallel spins.

V. CHANGES IN THE PHYSICO-MECHANICAL CHARACTERISTICS OF NIOBIUM CAUSED BY HYDROGENATION

The interaction of hydrogen with point and line defects and with grain boundaries and matrix atoms (hydride formation) produces a change in the physico-mechanical properties of the metal often accompanied by large-scale mechanical failure, even without externally applied loads. Thus it was reported [69,70] that the saturation of very pure rolled niobium with electrolytically generated hydrogen caused embrittlement of the sample. With Nb samples in wire form (0.3 mm diameter) containing $c_H \geq 0.03$ wt.% of hydrogen the onset of hydrogen embrittlement (which depends on the extent of the previous deformation ε) was found to be associated with the formation of a hydride phase. The hydrogen embrittlement increases for $\varepsilon \leq 5\%$, but as ε is further increased from 5 to 98% the embrittlement decreases. This has been attributed[70] to the formation of a cellular dislocation structure at high values of ε, whose rearrangement is hindered during hydrogenation.

Combined metallographic and X-ray diffraction studies[70] explained these changes in the mechanical properties of niobium as due to reversible distortions of the crystal lattice of the matrix during the first and the second hydrogenation stage, and to the formation of a hydride (Nb_xH_y) with a larger lattice constant during the third stage. Since its specific volume is greater than that of the matrix the hydride is concentrated along certain crystallographic directions <*hkl*> and produces large stresses (sufficient to cause spontaneous fracture of the metal when c_H is increased).

In some of the most detailed studies of hydrogen embrittlement[71,72] the effect in the Nb–H alloys was also associated with dislocation effects, resulting from the formation of hydride particles (precipitates) at the extremities of the resulting cracks. The hydrogen cracking is produced by the high internal stresses generated in the metal, and the hydride particles act as foci for the generation of breakdown, giving a high plasticity to the Nb–H alloys with a uniform distribution of particles. A study of the hydrogen embrittlement of niobium samples stretched within the column of the electron microscope showed that no embrittlement takes place at low c_H values, as also found in earlier investigations.[69]

A simple relationship between the increase in length of the hydrogen cracks $\Delta\tau_H$ and the characteristics of the hydrogen precipitates (hydride particles) has been reported:[73]

$$\Delta\tau_H = \frac{\pi r_B \gamma_0}{2bl_B} , \qquad (12)$$

where *b* is the Burgers vector of the dislocation, l_B is the distance between the hydrogen precipitates, r_B is their radius, and γ_0 is the surface energy of the hydrogen precipitate.

The hydrogen–dislocation interaction determines the growth of the crack during loads with an alternating sign, i.e. in the most hazardous conditions experienced in the practical application of niobium components operating in hydrogenating media. Experiments with foil samples of Nb at 293 K and a load cycling frequency of 4 Hz showed[74] that the liability to catastrophic breakdown increases with c_H.

In polycrystalline material the hydrogen embrittlement is strongly affected by impurities which can react chemically with hydrogen, as was stated above. Contamination of the niobium with oxygen or nitrogen (~0.1 at.%) raises the critical embrittlement temperature: the Porteven–Le Chatelier effect is clearly seen at 340–394 K in oxygen-containing samples[75]. It is due to the suppression of the motion of dislocations by the oxygen (Snoek) atmospheres. The interaction of oxygen with hydrogen should strongly influence this effect, partly because the hydrogen–dislocation interaction tends to retard the motion of dislocation in the hydrogen-saturated lattice, and partly because the increased mobility of the oxygen atoms in an anisotropically distorted hydrogenated lattice tends to oppose the effect.

The substitutional impurities V, Mo, and Ta (~3–5 at.%) have a dominant effect on the solubility of hydrogen (P_M) in niobium.[49] Vanadium impurities increase P_M most strongly, possibly because the interaction of hydrogen with substitutional impurities having a radius smaller than niobium is energetically favoured.[76] In this case the hydrogen decreases the deformation of the lattice. However, as was pointed out above, these systems (unlike those containing interstitial impurities) do not show direct M–H chemical interaction.

The effect of the distribution of impurities on the hydrogen embrittlement is stronger in polycrystalline than in monocrystalline samples.[76] For identical c_H values the differences in mechanical properties under tension between mono- and polycrystalline niobium samples are observable at 291–295 K, and the minima on the temperature dependences of the mechanical characteristics and of the internal friction are in similar positions. This is evidence that the hydrogen–dislocation interaction is responsible for the change in mechanical characteristics. The maxima in the temperature dependence of the mechanical characteristics near 300 K are also close to the maxima which characterise the γ peaks on the internal friction curves. Electron fractograms of the fracture surfaces of Nb mono- and polycrystals revealed fragmentation and cellular break,[7] typical of polycrystalline samples, at high c_H values. The formation of a "river pattern" on the fractogram in the presence of hydrogen embrittlement distinguished most of the tests at low temperatures (77 K).

Thus the change in mechanical characteristics of niobium is due to the rearrangement of the metal structure at a number of levels, initiated by the hydrogenation.

VI. ELECTROCHEMICAL ASPECTS OF THE PROBLEM

Let us now examine the corrosion-electrochemical behaviour of niobium in various electrolytes and the role in these processes of structural changes induced by hydrogenation.

1. Kinetics and Mechanism of the Corrosion-electrochemical Processes on a Niobium Surface in Acid Media

Electrochemical studies of niobium in acid media were begun only recently. Most of the published data refer to changes in the hydrogen overvoltage (η) on niobium in acid media. This is because niobium and its alloys are promising new materials for the electrolytic production of hydrogen by electrolysis of aqueous solutions. The dependence of the potential of an oxidised niobium electrode at 298 K on the pH of the solution can be expressed as

$$\varphi = \varphi^0_{Nb_2O_5/Nb} - 0.059\,\mathrm{pH}\,, \qquad (13)$$

which shows that this system can be used as an indicator electrode.[77] The equilibrium potential of the system in buffer media of pH ~ 2 is established in 15–20 min. It is reported[77] that after mechanical polishing or anodic surface treatment the niobium electrode can be used for potentiometric redox titrations in solutions of pH $\lesssim$ 10. The exact reversibility of the Nb–H binary system during hydrogenation cycles allows the Nb electrode to be used as an electrothermal resistor.[78]

The anodic characteristics of niobium (a valve metal whose oxide has semiconductor properties) and those of its alloys have been less extensively studied. The anodic oxide, as was stated above, plays a controlling role in metal–electrolyte exchange processes. Studies of Nb and Ni–Nb in the amorphous and the crystalline state have shown[79] that a defect-free oxide film having a high electronic conductivity is formed on the amorphous alloy. This allows the $Ni_{60}Nb_{40}$ alloy to exist in a stable passive state. In acid solutions niobium is easily passivated by anodic polarisation. According to Heusler[80] the stationary corrosion of Nb in the passive state is controlled by the structure of the oxide and depends on its rearrangement and erosion. The reforming of the oxide layer by electrochemical treatment is attributed[81] to the transport of ionic defects such as uncoordinated metal and oxygen atoms. These defects are formed on the metal–oxide and oxide–electrolyte interfaces, and their transport in the oxide layer takes place by the switching over of broken bonds on the metal and oxygen atoms.

In recent years Nb has been used in alloy making not only as a carbide-forming additive but also as a major component to assist austenitic grain growth and to give enhanced passivation.[82–86] As the Pourbaix diagram of the niobium–water system shows, oxide films on the niobium surface are unstable in alkaline solutions, and the niobium should corrode rapidly. Oxygen-covered Nb surfaces are strongly affected by anions (SO_4^{2-}, halides) and by surface-active species, which produce changes in the Nb–O bond energy. Thus, sulphur deposited on the niobium surface weakens the bond between adsorbed oxygen atoms and the surface very substantially. This can be explained[87] by assuming that the adsorption centres for oxygen and sulphur are the same.

Thus on the oxidised surface of a Nb electrode the adsorption of hydrogen is to a large extent reversible. The reversibility can be disrupted by the adsorption of anions from the electrolyte or of hydride-forming elements. Complete dissolution of the niobium oxide Nb_xO_y is possible only in a cathodic process far removed from equilibrium.

2. Electrochemical Characteristics of Niobium in the Cathodic Potential Region

Some of the earlier work[88–90] dealt with the hydrogen overvoltage on niobium and showed that the dependence of η on the cathodic current i_K and on the pH can be described by the slow discharge theory. For i_K = const we observe a strong time dependence of the potential ϕ: stabilisation occurs after 3 applications of cathodic polarisation lasting 1 h each. This is due mainly to the reduction of Nb_xO_y thin films during cathodic polarisation.

According to the polarisation measurements the nature of the alkali (NaOH, KOH, LiOH) has practically no effect on the overvoltage (unlike the concentration of the electrolyte).[90] Since the free energy of adsorption of atomic hydrogen on niobium is high, the hydrogen evolution reaction is rate-limited by the electrochemical desorption step:

$$H_2O + \bar{e}(M) \rightleftarrows H_{ads}M + OH^- \qquad (14)$$

$$H_2O + \bar{e}(M) + H_{ads}M \rightarrow 2M + OH^- + H_2 \qquad (15)$$

At surface coverages of the Nb by atomic hydrogen $\theta_H \cong 1$ the overvoltage equation is

$$\eta = k_{15} - \frac{1-\alpha}{\alpha}\cdot\frac{RT}{F}\ln a_{H_2O} - \frac{RT}{F}\ln a_{OH^-} + \frac{RT}{F}\ln i_K \qquad (16)$$

where a_{H_2O} and a_{OH^-} are the activity of water and of the hydroxyl ion respectively, F is the Faraday, α is the transfer coefficient, k_{15} is the rate constant of reaction (15), and R is the gas constant.

This equation is accurately consistent with experimental data:[91] the dependence of η on $\ln [a_{H_2O}^{\frac{1-\alpha}{\alpha}} \cdot a_{OH^-}]$ is linear, with a slope (b_K) close to the theoretical value. A discontinuous change in hydrogen overvoltage on niobium resulting from previous cathodic treatment of the surface has also been reported,[88–90] and attributed to the discrete change in lattice constant caused by hydrogenation and hydride formation. After lengthy hydrogenation (30 h at i_K = 100 A m^{-2}) the lattice constant a becomes stable, resulting in a steady value of η; at higher values of i_K the changes in η are more rapidly suppressed.

A study of the electrochemical properties of the interface between niobium and a sulphuric acid electrolyte showed[89] that as a result of cathodic polarisation the double-layer capacitance (C_d) on Nb rapidly rises (in 0.5 h for i_K = 100 to 250 A m^{-2}) from 50–60 to 80 μF cm^{-2}. This increase is attributed[89] to the reduction of the thin oxide layers formed on the metal as a result of previous anodic treatment rather than to phase transitions in the near-surface layer of Nb. The micro-hardness HV of hydrogenated Nb layers gradually increased, reaching a stable value 10–15 h after the beginning of the cathodic polarisation, which is consistent with the X-ray analysis results. Sudden changes in current (oscillations) in alkaline solutions are well known in efficiently passivated 4d metals. In this case the kinetic equation for the hydrogen evolution reaction becomes

$$i_K = i_0 \cdot \exp\left[-\frac{(1-\alpha)F\eta}{RT}\right] \qquad (17)$$

where i_0 is the exchange current. The oscillations of i_K often observed at high values of η are associated with ohmic changes in the near-electrode layer, i.e. with oscillations

in the resistance of the electrolyte layer resulting from the alternate accumulation of molecular hydrogen and of Nb^{3+} ions.[92]

A calculation of the activation energy of the dissolution of hydrogen in Nb in H_2SO_4 solutions by Gorbachev's temperature-kinetic method gave values of 44.0 [88,89] and 47.3 kJ $mole^{-1}$.[93] In this case the hydrogen evolution corresponds to the Volmer process

$$H_3O^+ + \bar{e}(M) \rightleftarrows H_{ads}M + H_2O \qquad (18)$$

Thus the kinetics and mechanism of the hydrogen evolution reaction on a Nb electrode surface are very dependent on the formation of a hydride phase in the near-surface layer. The mechanism of the elementary act is complicated by the change in electronic structure of the surface on which the hydrogen is adsorbed. The overvoltage of the hydrogen evolution reaction on the hydride depends on the degree of saturation of the near-surface layer with hydrogen and on the intensity of the cathodic process.

A recent review[94] discusses three possible mechanisms of the hydrogen evolution reaction on niobium. The first includes the Volmer process (18), which determines the rate of evolution of hydrogen, followed by the fast step (Heyrovsky–Horiuti process)

$$H_{ads}M + H_3O^+ + \bar{e}(M) \rightleftarrows 2M + H_2 \qquad (19)$$

The second mechanism consists of the fast Volmer reaction (18) followed by the slow step (Tafel process)

$$H_{ads}M + H_{ads}M \rightleftarrows 2M + H_2 \qquad (20)$$

This mechanism is controlled by the recombination of H_{ads}, and therefore the rate of hydrogen evolution is independent of the electrode potential. The third mechanism postulates a fast Volmer reaction (18) followed by a slow Heyrovsky–Horiuti reaction (19). In this case the cathodic current is described by the expression

$$i_K = k_c a_{H_3O^+} \cdot \exp\left[-\frac{(1-\alpha)F\varphi}{RT}\right], \qquad (21)$$

where k_c is the rate constant and $a_{H_3O^+}$ is the activity of H_3O^+. According to Eqn.(21) the slope of the polarisation curve is $(\partial\phi/\partial \lg i_K)_{pH,T} = 2.3RT/(1-\alpha)F$, and the order of the reaction with respect to OH^- ions is $(\partial \lg i_K/\partial\, pH)_{\phi,T} = 1$. These parameters apply to both polycrystalline and monocrystalline samples.

The adsorbed hydrogen can either be evolved from the metal surface or be transferred to an internally adsorbed state under the M electrode surface (*s* form), from which it can redistribute itself in the near-surface layer by diffusion:[95]

$$H_{ads}M \underset{k_{ads}}{\overset{k_{abs}}{\rightleftarrows}} H_sM \qquad (22)$$

Here k_{abs} and k_{ads} are the rate constants for the absorption of hydrogen by the metal and for its adsorption on the surface from the bulk of the metal.

In general the cathodic process leading to hydrogen evolution in acid media can be expressed as follows:[95]

$$H_3O^+ \xrightarrow[-H_2O;\,(a)]{\bar{e}(M)} H_{ads}M \begin{cases} \xrightarrow[-H_2O;\,(b)]{H_3O^+,\bar{e}} H_2 \\ \xleftarrow[(c)]{} H'_{abs}M \xrightarrow[(d)]{v_\alpha} H_{abs}M \xrightarrow[(e)]{} M + \tfrac{1}{2}H_2 \end{cases} \qquad (23)$$

Here v_α is the diffusional flow of hydrogen atoms into the bulk of the metal; $H'_{abs}M$ and $H_{abs}M$ denote an absorbed hydrogen atom on the metal surface and under it respectively. Some of the hydrogen forms molecules and emerges into the electrolyte, whereas the remainder penetrates into the metal where it can either form a solid solution or be bound in a hydride phase. It was suggested[69] that step (*c*) in Eqn.(23) is at equilibrium, i.e. that the hydrogen adsorbed in the *s* state is removed by electrochemical desorption according to Eqn.(19). In the case of the hydrogen absorbed by the metal two situations can arise: 1) the whole of the absorbed hydrogen is present in the bound (hydride) form, or 2) a chemical M–H bond is not formed, and supersaturation of the near-surface layer initiates the desorption process [step (*e*)], in which the hydrogen is returned to the metal–electrolyte interface where it undergoes electrochemical desorption by reaction (19).[96] Lastly, these two processes can occur simultaneously, producing a quasi-equilibrium state characterised by the slow breakdown of the hydride layer with evolution of hydrogen at the metal–electrolyte interface. We should stress that the hydrogen in solid solution is not desorbed from the entire surface of the metal but only from some specific active centres (usually, line or plane defects on the metal surface).

In the formal kinetic treatment of the scheme (23) the ratio of the rates of certain steps should affect the overall balance of hydrogen absorbed by the metal and hydrogen removed electrochemically. Experimental data for the hydride-containing metal agree well with mechanism of hydride layer formation followed by binding of the absorbed hydrogen in the hydride. In a hydrochloric acid solution the parameter b_K increases as a result of hydrogenation.[88,89] A study of the frequency dependence of the impedance[89] suggests that step (*c*) could be treated as a heterogeneous chemical reaction.

The general conclusion from this Section is that for low c_H in the near-surface layer (and correspondingly short cathodic polarisation times) the rate of the hydrogen evolution reaction is controlled by the slow discharge step (18). For longer cathodic processes (i.e. for high levels of hydrogenation) we must allow for the formation of Nb–H chemical bond, the decrease in the Fermi energy E_F, and the "ennoblement" of the metal resulting from the filling of the *d* band of the transition metal by the *s* electrons of the hydrogen. The decomposition of the supersaturated solid solution or the dissociation of the Nb_xH_y hydride influences the electrochemical process on the metal surface, causing an increase in the rate of formation of hydrogen molecules and possibly also in the rate of electrochemical desorption of the hydrogen.

3. Electrochemical Characteristics of the Niobium Electrode During Anodic Polarisation

Let us now examine the anodic process coupled with the hydrogen evolution reaction. The main process during anodic polarisation is the formation of an oxide layer on the anode. The initial stages of the reaction of oxygen with a clean monocrystalline niobium surface were studied[97] by a molecular beam method, which gave the changes in the sticking coefficient of the oxygen atoms (the ratio of the total number of sorbed oxygen atoms to the number of metal surface atoms on the (110) niobium face) as a function of θ_H and *T*. The adsorption of oxygen on the (110) face was shown to be a complex, multi-stage process, controlled by the diffusion of oxygen atoms into the bulk of the crystal. Thus on the most densely packed (110) face of niobium the adsorption of oxygen in the *s* state is possible only at high coverages of the surface by oxygen (θ_0), and its requires cooperative lateral displacements of the first layer of Nb atoms. At low θ_0 values a very thin ($l \cong 0.5$ nm) layer of oxide (Nb_xO_y, $x = 1$, $y \leq 1$) is first formed on a clean polycrystalline or monocrystalline Nb surface at 293–295 K, and this initial layer is converted into Nb_2O_5 when $l > 2$ nm.[98]

The growth of oxide films showing ionic conduction in electrolytes under anodic conditions is the result of a chemical diffusion process in an oxide of non-stoichiometric composition. Ionic transport in the growing oxide layer has been attributed[81] to the motion of positive or negative NbO_2^+ and NbO_2^- ions by the "switching over" of broken bonds on the oxygen and niobium atoms. The NbO_2^+ ions are formed at the metal–oxide interface, and the NbO_2^- ions at the oxide–solution interface. The kinetics of the formation of a layer of oxide on the anode are determined to a large extent by external conditions in the electrolyte (parameters of the anodic treatment, pH and concentration of the solution).

After a long cathodic treatment a layer of hydrides is formed on the niobium surface by the percolation mechanism. This process is hindered by non-uniform reduction of the oxide layer. An ellipsometric study[99] of changes in oxide films formed in air or by anodic oxidation of a niobium electrode, and of changes in the hydride layer previously formed by cathodic treatment over a wide range of electrode potentials, has been reported.

A study of the formation kinetics of anodic oxide on niobium by the capacitance method[100] in dilute solutions of salts, acids, and bases has shown that the formation potential of the oxide (ϕ_{ox}) is linearly time-dependent at 293–333 K. It was established[100] that under conditions of 100% current yield the thickness l of the oxide film increases according to the Young equation

$$l = k\varphi_{ox} \qquad (24)$$

during the anodic oxidation, and that the rate constant of the formation k = 2.6 nm V^{-1} depends on the temperature and on the anodic current density i_a. Anodic polarisation of a Nb electrode covered with a layer of hydrides results in dissociation of the hydrides and formation of a new oxide layer. Cathodic polarisation of a Nb electrode bearing an anodic oxide layer does not immediately regenerate a layer of hydrides under the oxide layer. According to Auger spectral results a thin oxide layer may persist over the hydride layer even after lengthy cathodic treatment.[99] The rearrangement of the anodic oxide during hydrogenation has been interpreted[101] as an electron–proton reaction with a decrease in the valency of Nb:

$$Nb_2O_5 + H_3O^+ + \bar{e} \rightarrow Nb_2O_4OH + H_2O \quad . \qquad (25)$$

The intermediate formed by reaction (25) is characteristic of the anodic treatment of Nb in alkaline solutions, since the discharge of hydrogen ions during the cathodic process increases the electronic conductivity of the Nb_2O_5 oxide: in these circumstances we must also allow for the electron-acceptor nature of the Nb^{4+} ions.

Anodic oxidation of a Nb electrode in alkaline KOH solutions leads to the formation of niobium dioxide NbO_2 as well as Nb_2O_5 on the surface.[102] Shatalov and co-workers[103] formed anodic oxides in 1 *N* solutions of HCl, HNO_3, H_3PO_4, and H_2SO_4, and they showed that the polarisation of the Nb electrode increases with time for a constant i_a. The most perfect anodic oxide layer was formed in a phosphoric acid solution, where the high electric fields needed to enhance the protective action of the Nb_xO_y are produced by changes in E_a rather than by the penetration of PO_4^{3-} into the oxide layer. However, the anionic composition of the solution during the anodic polarisation of niobium has a marked effect on the chemical composition of the anodic oxide layer. It has been reported[104] that the anodic layer produced in a 10 M H_3PO_4 solution at $i_a = 10^4$–10^6 A m^{-2} contains phosphorus impurities (up to 95 gm cm^{-2}). The partial inclusion of PO_4^{3-} ions in the anodic oxide layer is probably responsible for its high structural perfection. The anodic dissolution process is fastest in solutions containing F^- ions, since under these conditions the oxygen in the anodic layer is replaced by F^- (which has a higher affinity for Nb). The rate of dissolution of niobium fluorides is also high.

Some interesting aspects of the anodic behaviour of the $Nb_{25}Ni_{75}$ alloy in sulphuric acid solutions were observed in that work.[104] Separately, both nickel and niobium readily dissolve in sulphuric acid solutions containing halide ions (Hal^-) under anodic polarisation. However, their alloy is rapidly passivated in the same solutions. It is suggested[104] that the Nb atom is oxidised while still in the metal lattice, which lowers its activity (since NbO_2^+ has a low activity), so that the atom does not go into solution but is retained on the surface, forming a passivating oxide film. This film consists of a mixed oxide whose composition and properties are determined by the corrosion-kinetic characteristics of the components.

Alloying the niobium with noble-metal additives should make the passivating oxides chemically even more unreactive and should lower the rate of the anodic process.[105] Adding the Cl^- ion to the electrolyte increases i_a. Adding C_2H_5OH to an acid aqueous solution containing Hal^- ions lowers the number of activating anions which are adsorbed and incorporated into the anodic oxide film.[106] Accordingly, the addition of water to alcoholic bromide solutions increase the rate of the active dissolution of Nb, whereas the addition of C_2H_5OH to aqueous solutions suppresses it. A totally passive state of the Nb electrode can be obtained at some well defined ratios of alcohol to water.

The rate of anodic dissolution is very dependent on the pH. It was shown[107] that at pH > 11.3 the current i_a is almost independent of the concentration of ions ($c_{H_3O^+}$). The process is controlled by reactions (14) and (15), and its rate at $\theta_H \rightarrow 1$ can be calculated by Eqn.(21).

Thus during the formation of an anodic oxide layer the anions present in solution (especially Hal^- ions) can penetrate into the layer and affect the corrosion resistance of niobium and its alloys. The chemical affinity of the anion from the solution towards niobium is mainly responsible for determining the corrosion resistance of the metal in aggressive media: the chemical resistance of Nb can be increased not only by bulk doping but also by surface doping with cathodic additives. The near-surface layers of anodically treated Nb can be doped from acid solutions containing Mo, W, Cr, or Zn impurities, which enhance the protective action of the anodic oxide layer on Nb.[108]

4. Corrosion Behaviour of Niobium in Acid Media

Relatively few experimental results on the corrosion behaviour of niobium and its alloys in aggressive media have been published. In a study of the corrosion of Nb in aqueous hydrochloric acid solutions[109] the rate of corrosion K was found to decrease with time. When the temperature is raised from 305 to 373 K the parameter K initially increases about 20-fold, but 60 days after the beginning of the corrosion process K becomes almost independent of T (10 μm day^{-1}). In this temperature range Nb was classified as an absolutely stable metal in 1 *N* HCl solution.[109] The activation energy for dissolution in the HCl/Nb system is 50–90 kJ $mole^{-1}$. The changes in physico-mechanical and corrosion-electrochemical characteristics of Nb caused by hydrogenation without formation of hydride phases do not markedly affect the corrosion resistance of niobium in media of pH > 1, and they may even increase it slightly.[110]

The corrosion resistance of binary alloys based on niobium and of alloys doped with cathodic additives can be much higher than that of pure Nb. Thus a study[111] of the corrosion resistance of binary Nb–Ta alloys has shown that in H_2SO_4, HCl, and HNO_3 solutions these materials are in a passive state over a wide range of potentials and temperatures (373–523 K). This result was subsequently confirmed.[112] The corrosion stability of Nb–Ta alloys can be increased by high-temperature heat treatment, which produces a mixture of Nb and Ta pentoxides on the surface. The chemical inertness of β-Ta_2O_5 containing Nb is substantially higher than that of β-Nb_2O_5 containing Ta. Up to 50 at.% of niobium can be added without significantly impairing the corrosion resistance of tantalum.[112] By additionally doping these alloys with palladium or platinum we can produce constructions materials for the protection of systems operating in very corrosive media.

The corrosion resistance of niobium alloyed with ruthenium and molybdenum is discussed in Refs.113 and 114. Alloying with ruthenium lowers i_a and widens the region of potential in which the passive state is preserved. Measurements of the weight loss of these alloys in 1–10 *N* solutions of H_2SO_4 have shown that the rate of corrosion is extremely low: 10^{-4} mm year^{-1} ($\sim 3 \times 10^{-4}$ μm day^{-1}).[113] Thus the corrosion stability of niobium and its alloys in hydrochloric acid solutions is slightly worse than in sulphuric acid solutions. This is due to the effect of Hal^- ions on the structure and properties of the oxide films on niobium; the SO_4^{2-} ion has a very much lower surface activity.

The rate of corrosion of niobium can be decreased by alloying it with 5–10 wt.% of molybdenum or tungsten. In 4% H_2SO_4 $K = 2.2$ g m^{-2} h^{-1} for pure niobium, and 0.2–0.4 g m^{-2} h^{-1} for Nb–Mo and Nb–W alloys. However, these binary alloys have a low plasticity and require additional alloying. The addition of small quantities of zirconium (0.003–0.1 wt.%) worsens the plasticity but further improves the corrosion resistance by producing oxide layers with a more perfect structure.

The Zr + 2.5 at.% Nb alloys, whose corrosion resistance has been extensively studied,[116] is widely used in nuclear energetics and in various branches of technology. These concentrations of niobium produce a significant loss of corrosion resistance in the zirconium. Furthermore the ease of hydrogenation decreases in this alloy. Thus the Zr + 2.5 at.% Nb has some advantages over the Zircalloy-1 and Zircalloy-2 materials from the point of view of hydrogen embrittlement, but its chemical stability is inferior. This is because of the structural aspects of the oxide films discussed above. The search for effective corrosion inhibitors for this alloy is now an important problem.

5. Effect of Anions from the Solution on the Corrosion Behaviour of Niobium in Acid Media

The Hal^- ions have the strongest influence on the structure of the passivating niobium oxide layers. The passivating film is "infected" by the activating halogen ion,[116] and this lowers the active dissolution potential. Several studies of these processes have been reported, and the F^- ions are invariably found to be the most active depassivators of all the halide ions.

In the anodic dissolution of niobium in sulphuric acid electrolytes containing HF additions the following chemical and electrochemical processes on the anode have been suggested:[117–119]

$$Nb \xrightarrow{n\bar{e},H_2O} Nb_2O_n \xrightarrow{HF} H_2NbO_xF_{(7-x)} \xrightarrow{HF,H_2SO_4} HNbF_6, \quad (26)$$

with x decreasing from 7 to 0 with increasing distance from the metal surface. It follows from (26) that a film of niobium oxide fluoride is formed on the Nb electrode surface. Its formation is accompanied by oscillations of the current in the anodic polarisation curves. The parameter n varies between 4.65 and 4.95, i.e. non-stoichiometric niobium oxides (with poor dielectric properties) are formed. The formation of a layer of Nb_2O_5 depends on the rate of supply of oxygen to the electrode surface and requires currents higher than the limiting current. In media containing Hal^- the cathodically activated Nb electrode dissolves more rapidly. The previous cathodic polarisation increases the pH of the layer of solution adjacent to the cathode and thus helps the formation of an oxide structure more permeable to cations, resulting in a rapid decrease in K.[120]

In acid media Cl^- ions cause a loss of dielectric properties in the surface anodic oxides of niobium, obviously through the replacement of O by Hal^- in the film. The effectiveness of the discharge of Cl^- ions on the surface of the $Ni_{60}Nb_{40}$ alloy is increased by amorphisation of the alloy, which thus increases the chemical stability of the alloy in chloride solutions.[81] Anodic polarisation of niobium in a hydrochloric acid solution containing 0.05–10 mole litre^{-1} of Cl^- lowers the effectiveness of the growth of the oxide film, the depassivating action of the adsorbed Cl^- ions being suggested[121] as an explanation.

The multi-step character of the dissolution of niobium is pointed out in many papers. The most obvious manifestations are the rearrangements in the anodic oxide layers on standing, caused by the desorption of electrolyte species. More complex electrochemical systems, containing various organic molecules in addition to solution anions, suppress the activation of niobium in Hal^- ions.[106,122] Thus, Br^- ions in aqueous solutions containing CH_3OH result in the formation of soluble $[Nb(OCH_3)_mBr_n]^{p+}$ complexes. The adsorption of organic molecules (for example, corrosion inhibitors) decreases the incorporation of active halide ions in the anodic oxide layer and thus it also lowers the constant K.

Thus halide ions can produce local depassivation of the Nb surface, which can take place on active centres with a low adsorption energy. The practical importance of this effect is obvious, since the great majority of assemblies, components, and apparatus used in the chemical industry are exposed to hydrogenating media containing halogen ions.

The decrease in the corrosion resistance of niobium and its alloys is strongly dependent on structural changes in the passivating oxide layer, which is itself determined by the distortion state, the concentration, and the topology of the defects in the near-surface layer, and by the crystallography of the corroding surface. Hydrogenation not only assists the dissolution of the oxide layers but also induces substantial disorder in the near-surface layer, resulting from the active interaction of the hydrogen with the defects in the metal. Further theoretical and experimental studies of the rearrangement of the surface as a result of hydrogenation and phase transitions in the near-surface layers are needed.

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