NITRIDING OF METALS AND INTERACTION OF THE NITRIDES WITH A LOW PRESSURE HYDROGEN PLASMA

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ABSTRACT

The kinetics of nitriding of metals in a low pressure nitrogen plasma represents a complex phenomena which cannot be described by a simple diffusion equation. As an example both experimental results and a theoretical model of nitriding of titanium are presented.

Remarkable segregation processes are observed by nitriding of stainless steel at temperatures between ~ 300 and 650°C.

Titanium and niobium nitrides appear stable upon exposure to hydrogen plasma at temperatures up to ~ 700°C and fluences up to about 5×10^{24} H atoms cm^{-2}. In contrast, a quantitative depletion of nitrogen from nitrided stainless steel surface exposed to the hydrogen plasma is observed at temperatures as low as ~ 360°C.

The permeability of atomic hydrogen into titanium and niobium is strongly reduced by a properly formed nitride layer.

1. INTRODUCTION

The interest in nitriding of metals for surface hardening and other technological applications is well known (see e.g. [1]). Recently it has been suggested by Gruen and co-workers that a surface modification such as nitriding could be used in order to improve the efficiency of a divertor in the

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TOKAMAK devices for controlled thermonuclear fusion [2]. Both these aspects represent the motivation of the present work. Therefore it is desirable to study the kinetics of the nitriding at relatively low temperatures as well as the properties of the nitrided surfaces, in particular their stability in a hydrogen plasma.

In this paper we shall briefly summarize the results obtained on nitrided titanium and stainless steel. Because of the limited space available the reader is refered to the original literature for further details on the experimental set up and method used.

2. NITRIDING OF TITANIUM AND STAINLESS STEEL

2.1. Titanium

The "ion nitriding" of titanium in a D.C. discharge has been recently studied by Ming-Biann Liu, et al [3]. Konuma and Matsumoto [4] have performed a similar work using an R.F. discharge with the sample at a floating potential. Wirz has done a detailed kinetic and crystallographic study of the nitriding of several metals including titanium [5]. Using R.F. power up to 4 kW at ~ 1 MHz in a discharge tube of an inner diameter of 9.2 cm, sample temperatures up to ~ 800°C at a pressure up to ~ 2 torr were accessible in pure nitrogen without auxiliary heating. Careful kinetic measurements have revealed that even for thick specimens the rate of nitriding can be approximated by the $\sqrt{t}$-dependence only within a limited period of time. This is not surprising since many metals, such as Ti, Mo, Nb and others form several crystallographic phases of different stoichiometry which are, during the nitriding, sequentially formed. Since the diffusion coefficients of nitrogen vary in different phases, and even in a given phase they may be concentration dependent, deviations from the simple $\sqrt{t}$-law are to be expected.

Let us illustrate this point by the following example: Curve a in Fig. 1 shows the calculated depth profile of the nitrogen concentration in titanium nitrided in a nitrogen plasma at 700°C for a period of 25 hours (see [6] for details). In view of the absence of relevant published data the diffusion coefficients were considered to be independent of concentration. The calculated thicknesses of the individual phases agreed reasonably with the measured values [6]. A measurement of the nitrogen concentration profile by means of Rutherford-Back-Scattering technique (RBS) indicated that the actual nitrogen profile followed closely the calculated one up to a relative concentration of about 0.55, i.e. a composition of Ti_2N_{1+x}, where it levelled off (see Fig. 1, curve b). Since the exact determination of the concentration profile of a light element in a thick heavy matrix by this

technique is a rather appreciable task the results represented by curve b in Fig. 1 should be considered as preliminary. Nevertheless they are in agreement with similar measurements performed on nitrided molybdenum by means of Auger Spectroscopy during sputtering of the sample (see Fig. 2). With increasing depth the layer of a rather small gradient of the nitrogen concentration is followed by a region of a stronger decrease of the nitrogen concentration as indicated by broken line b' in Fig. 1. Unfortunately, such a depth was not accessible to the measurement by the RBS technique in the present experiments. Nevertheless this is clearly seen in Fig. 2 for nitrided molybdenum.

We should like to suggest as a preliminary interpretation that the difference between the measured and calculated depth profiles indicate a rather strong dependence of the diffusion coefficients on the nitrogen concentration when the latter approaches some critical value. This is also supported by the results of kinetic measurements shown in Fig. 3. The initial part of the curve which corresponds to the formation of the ε-Ti_2N phase can be described by a simple kinetic equation with a rate constant of $k = (1.6\pm0.7)\times10^{10} \exp - [44'200\pm 400/RT]$ $g^2cm^{-4}s^{-1}$. The activation energy is in reasonable agreement with the literature data on the diffusion of nitrogen in α-Ti [7] (E_{act} in cal $mole^{-1}$).

Details on the kinetics of the nitriding of <u>niobium</u> and <u>molybdenum</u> can be found elsewhere [5].

2.2. <u>Stainless Steel</u>

A detailed kinetic study of the nitriding of stainless steel is in progress. The nitriding proceeds at rates orders of magnitude higher than those for titanium. For example, a weight increase of about 1.8 mg cm^{-2} corresponding to a $\sim$25 μm thick nitride layer, has been found after nitriding of stainless steel No. 304 at 550°C and 0.8 torr for about 30 min.

The interpretation of the kinetic data is complicated by strong segregation processes occuring during the nitriding as shown in Table 1.

The data shown in Table 1 were obtained by means of X-ray Photoelectron Spectroscopy (XPS) using Mg K_α radiation. The relative accuracy was estimated to be of several %. One notices that nitriding at $\sim$ 670°C leads to a strong enhancement of chromium in the nitrided layer whereas iron richer nitride is obtained at a lower temperature. These segregation processes are not limited only to the surface but they spread into the bulk.

It should be emphasized that such effects will have signifi-

cant impact on the mechanical and corrosion properties of the steel nitrided at relatively low temperatures.

	Cr	Fe	Ni
untreated	23	64	13
nitrided at 670°C	89	5	6
nitrided at 475°C	23	71	6

Table 1

Changes of the surface composition (in weight %) of stainless steel No. 304 during nitriding at 670 and 475°C for a period of 1 hr and 1 hr 43 min, respectively. Besides chromium, iron and nickel the sample contained some carbon, silicon, phosphorus, sulphur and manganese (a total concentration of ~1 %) which were neglected here. The measured concentration of Cr, Fe and Ni agree with the data of the manufacturer.

3. INTERACTION OF NITRIDED METALS WITH HYDROGEN PLASMA

Two methods were used for the study of the stability of the nitrides in a low pressure hydrogen plasma: Measurement of weight changes of the samples due to hydriding, and the RBS-technique. The weight changes give only an approximate idea on the stability because of the diffusion of hydrogen into the sample which is more or less pronounced, depending on the metal and nitriding conditions (see [6]). The RBS-technique appears particularly suitable for this purpose since it is non-destructive and it possesses a high sensitivity. Figure 4 shows RBS-spectra of two nitrided titanium samples. Curve "N" corresponds to a sample which has been nitrided only (~1.6 torr, 700°C), curve "N+H" was measured on a sample which was, after nitriding under the same conditions, treated in a hydrogen plasma (1 torr, ~650°C, total fluence of thermal atoms $\geq 5 \times 10^{23}$ cm^{-2}, that of ions being a factor of ~ 10^4 less). The nitrogen content in the surface layers of both samples is compared by comparing the ratios $(A_2-A_1)/A_1$, A_1 and A_2 being the areas as indicated in Fig. 4. It turned out that these ratios are equal for both samples within the limits of accuracy of measurements, i.e. 0.3 % (see [6] for further details).

Thus we conclude that an exposure of titanium nitrided at ~700°C to a hydrogen plasma at ~ 650°C does not lead to any measurable attack of the nitride surface layer.

So far we could not study sputtering by ions in the 0.1 to several keV range. Preliminary experiments with irradiation by 1-2 MeV ions showed blistering to occur at doses typical for the appearance of the blistering for most metals.

Figure 5 shows RBS spectra of stainless steel 304-samples treated in a similar way: "N" - nitrided at ~ 620°C for 8 hr 35 min, "N+H" - nitrided under the same conditions and subsequently hydrided at ~ 630°C for ~ 3 hr. "SS" - is the RBS spectrum of an untreated sample.

First of all one notices local minima which occur in the spectrum of the nitrided sample just behind the metal- and nitrogen edges. They are probably due to some segregation effects as shown above (e.g. a carbon rich layer under the surface?).

A comparison of curves "N" and "N+H" shows a strong depletion of nitrogen within a surface layer of about 1 μm. Similar results were obtained also for samples which were exposed to the hydrogen plasma at much lower temperatures, e.g. at ~360°C.

Thus we conclude that nitrided steel is readily reduced by the low pressure hydrogen plasma even at relatively low temperatures.

This finding has to be taken into account also if a nitrogen reinforced steel should be considered for application in TOKAMAK devices.

4. DIFFUSION OF HYDROGEN INTO THE NITRIDED METALS

We have found that a few μm thin layer of nitrided titanium reduces the diffusion of hydrogen into the metal by a factor of 100 or more. This seems to apply for samples nitrided below the temperature of the $\alpha \leftrightarrow \beta$ phase transition. These results will be published elsewhere [6].

A similar effect has been found also for the nitriding of niobium. This work is still in progress and the results will be published later on.

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FIGURE CAPTIONS

Fig. 1: A calculated - curve a - and a measured - curve b - relative concentration of nitrogen in titanium. The broken line b' has been estimated from the measured depth profile of the microhardness. The surface composition, C_o, corresponds to TiN.

Fig. 2: Concentration profile of nitrogen in nitrided molybdenum measured by means of Auger electron spectroscopy and ion sputtering. The actual surface composition was MoN (δ-phase), whereas the apparent one is rather $MoN_{0.85\pm0.05}$ due to a preferential sputtering of nitrogen. Conditions of nitriding: ~ 1 torr, 850°C, 6 hr. C/Co and x in arbitrary units.

Fig. 3: Time dependence of the weight increase, ΔG, of a 5 μm thick Ti-foil during nitriding of titanium. The quadratic plot, ΔG^2, shows a change of the kinetics when the theoretical composition Ti_2N (indicated by arrows on the ordinates) is approached (see Fig. 3.b; 1.6 torr, 728°C).

Fig. 4: Rutherford backscattering spectra of two nitrided titanium samples: "N" - nitrided only, "N+H" - nitrided and then hydrided. 2 MeV-H^+, θ = 165°.

Fig. 5: Rutherford backscattering spectra of stainless steel 304: "SS" - sample as received, "N" - nitrided only, "N+H" - nitrided and then hydrided. 2 MeV-H^+, θ = 165°.

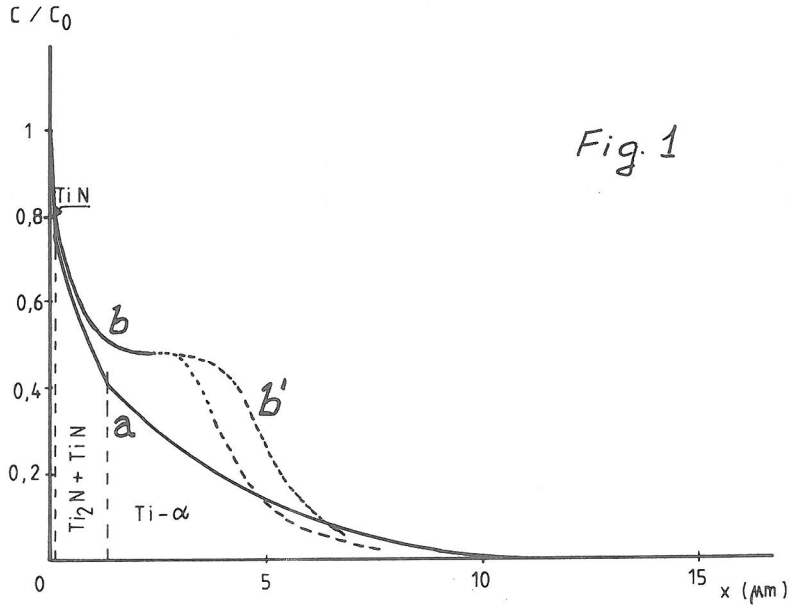

Fig. 1

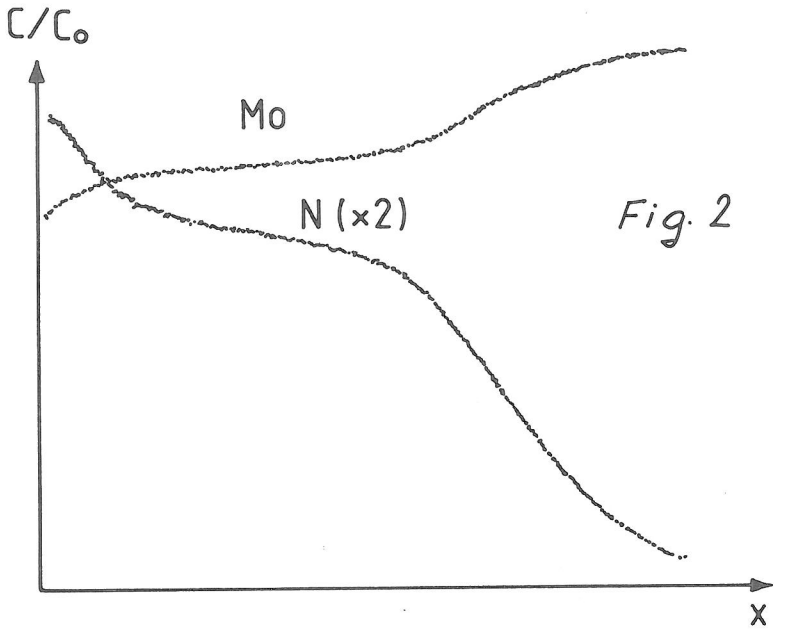

Fig. 2

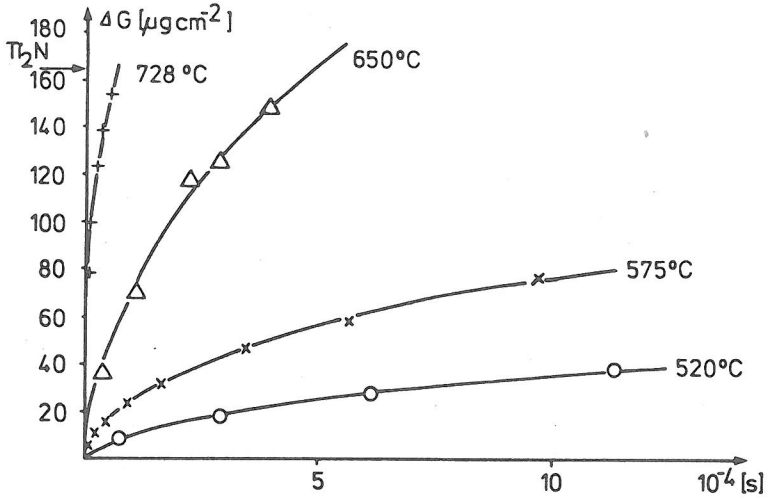
ΔG [μg cm⁻²]
180
Ti2N
160
140
120
100
80
60
40
20
728 °C
650°C
575°C
520°C
5
10
10⁻⁴ [s]

Fig. 3a

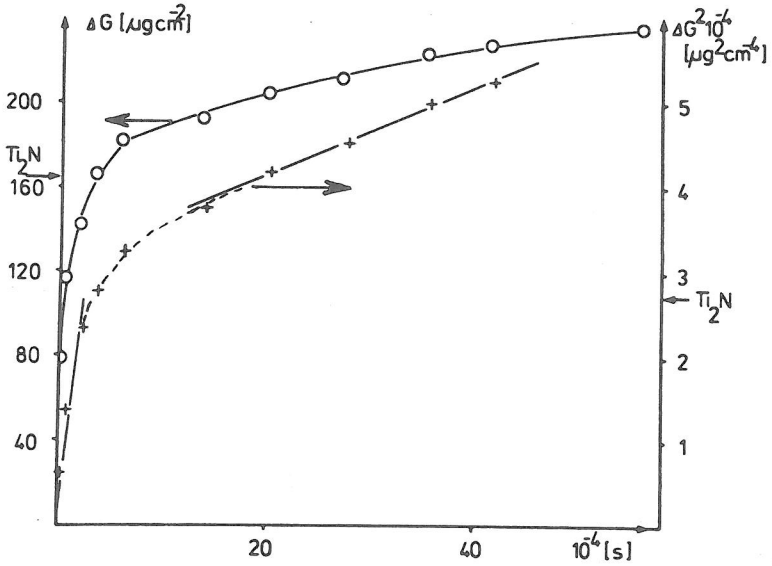
ΔG [μg cm⁻²]
ΔG² 10⁻⁴ [μg² cm⁻⁴]
200
Ti2N
160
120
80
40
5
4
3
Ti2N
2
1
20
40
10⁻⁴ [s]

Fig. 3b

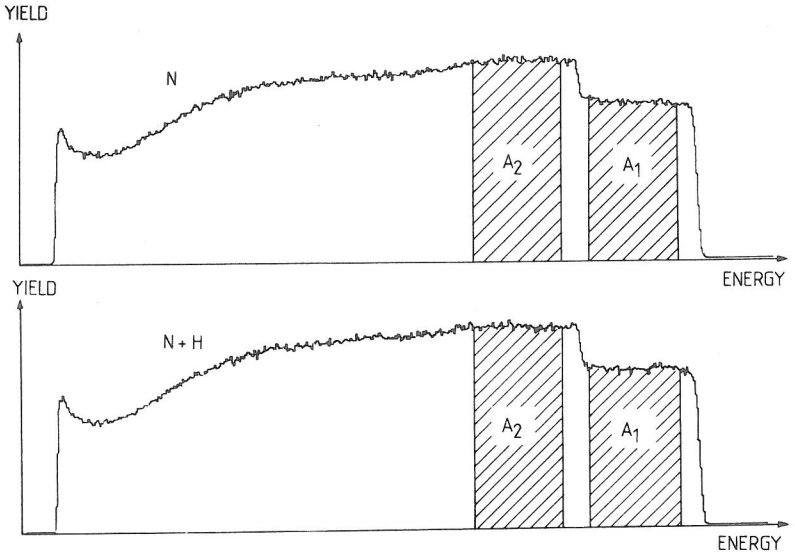

Fig. 4

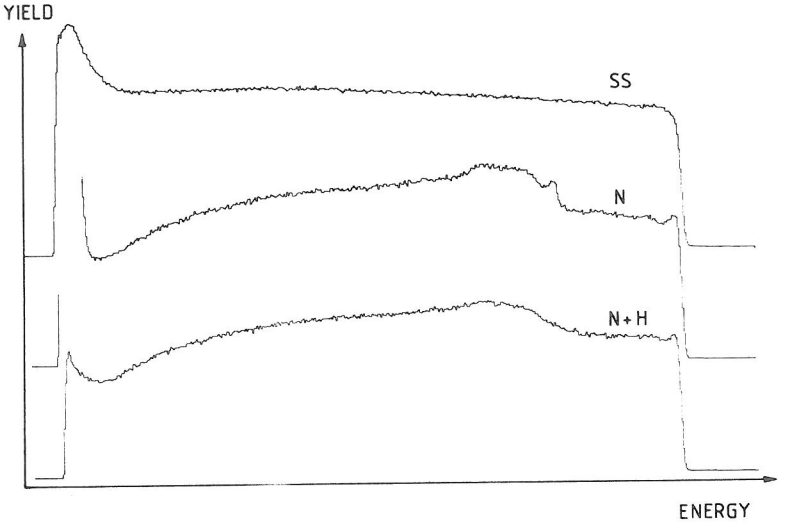

Fig. 5