

FIM-INVESTIGATIONS OF H₂, N₂ AND O₂ INTERACTIONS WITH THE
NIOBIUM SURFACE

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Introduction

The field ion microscope is a unique technique to study the interactions of light gases with metal surfaces in atomic resolution, especially the initial stages of physical and chemical reactions. Although the gas atoms themselves cannot be imaged in the FIM directly they are able to influence the field evaporation, field ionization and imaging process in a field ion microscope in a very sensitive manner. (1) (2) Their concentration at the surface and their depth profile in surface zones as well as their physical and chemical adsorptions on the metal substrate can additionally be controlled by the FIM atom probe. (3) In this context niobium is an ideal refractory metal for such surface investigations because it can well be outgassed in ultra high vacuum at sufficient high temperatures and can then dissolve high concentrations of hydrogen, nitrogen and oxygen in different concentrations depending on the external gas pressure p and the temperature T . In first approximation for low concentrations c Sieverts equation is valid $\lg c = \frac{1}{2} \lg p - A + B/T$. The values of the constants A and B can be found for instance in reference (4).

If mixtures of the light gases are present together with carbon monoxide or other carbon compounds the situation becomes more complex by formation of carbides with melting points surpassing that of niobium especially in case of higher carbon concentration. The presence of carbon has therefore been avoided as far as possible.

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Results and Discussion

Among the light gases hydrogen is distinguished by its much higher solubility and diffusion coefficient in niobium (5) especially at low temperatures compared with oxygen and nitrogen which is advantageous for FIM studies. In this case hydrogen gas supply for FIM imaging is possible not only from the external gas phase but also from inside the metal tip (6). This allows FIM studies in UHV at some elevated temperatures or on hydrogen promotion of field evaporation and field ionization and also FIM imaging with noble gases at lower field strengths. The absorption of hydrogen in niobium can be achieved either by etching the tip in a melt of 5 KOH + 1 NaNO₂ or in 9 HNO₃ + 1 HF or by heating the sample at sufficient high temperature (~600°C) with subsequent slow cooling in hydrogen at pressures below 1 bar.

Fig.1 shows a histogram got with a ToF atom probe for a niobium tip with a 40% hydrogen content.

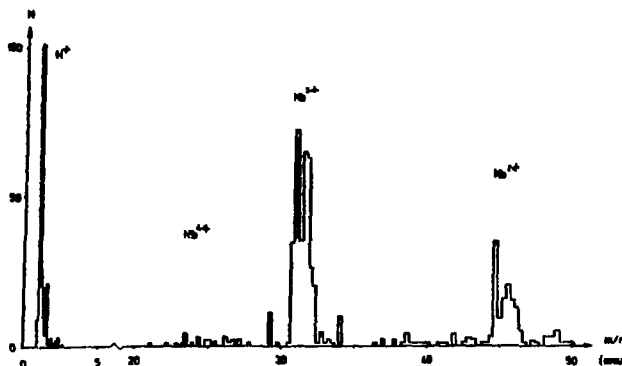
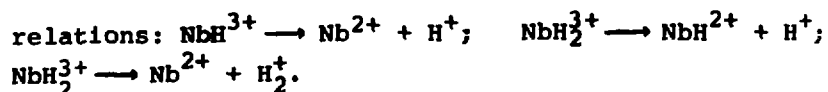


Fig.1

One sees that field desorption at higher pulse voltages occurs mainly as Nb³⁺ with only a slight amount of Nb²⁺ and Nb⁴⁺. Triple charged niobium hydrides formed dissociate in the high field region in front near the tip in the same way as known for tantalum (7) according the following

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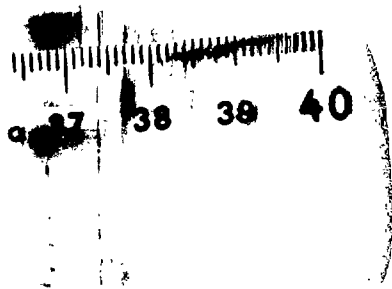


The broadening of peaks in the mass spectrum can be explained by premature field evaporation and therewith corresponding energy deficits of the desorbed ions.

Of special interest is the possibility to observe the extension of the well known hydrogen promotion effect from distinguished areas all over the tip surface as shown in Fig.2 a-e when 1% hydrogen has been added during imaging of the niobium tip with neon. The added hydrogen is first field induced adsorbed around the $22\bar{2}$ pole on the left side of Fig.2a as indicated by arrows and dashed lines which then extends continuously with increasing voltage over the whole tip Fig.2b-e. After removing most of the neon the tip has then been imaged with hydrogen Fig.2f showing many well resolved net planes.

If the hydrogen is not supplied from the gas phase but from inside the specimen in insufficient concentration localized or moving dark patterns have been observed. Different explanations have been taken into account. In principle dark areas are the result of lower local field strengths and therewith of lower local ionization probability caused partly by less conductive deposits with higher work function or by the missing of hydrogen adsorption at such areas. Since the hydrogen promotion effect is ascribed to adsorbed atoms or molecules in a first layer (8) at suitable field strengths it is assumed that the dark areas are mainly caused by the desorption of adsorbed hydrogen or metal hydride ions.

Whereas small additions of hydrogen to neon decrease the field evaporation and imaging voltage and improve the FIM imaging of niobium small addition of oxygen and nitrogen affect severe corrosions in surface zones yet enhanced by thermo- and electrotransport by high electric fields.



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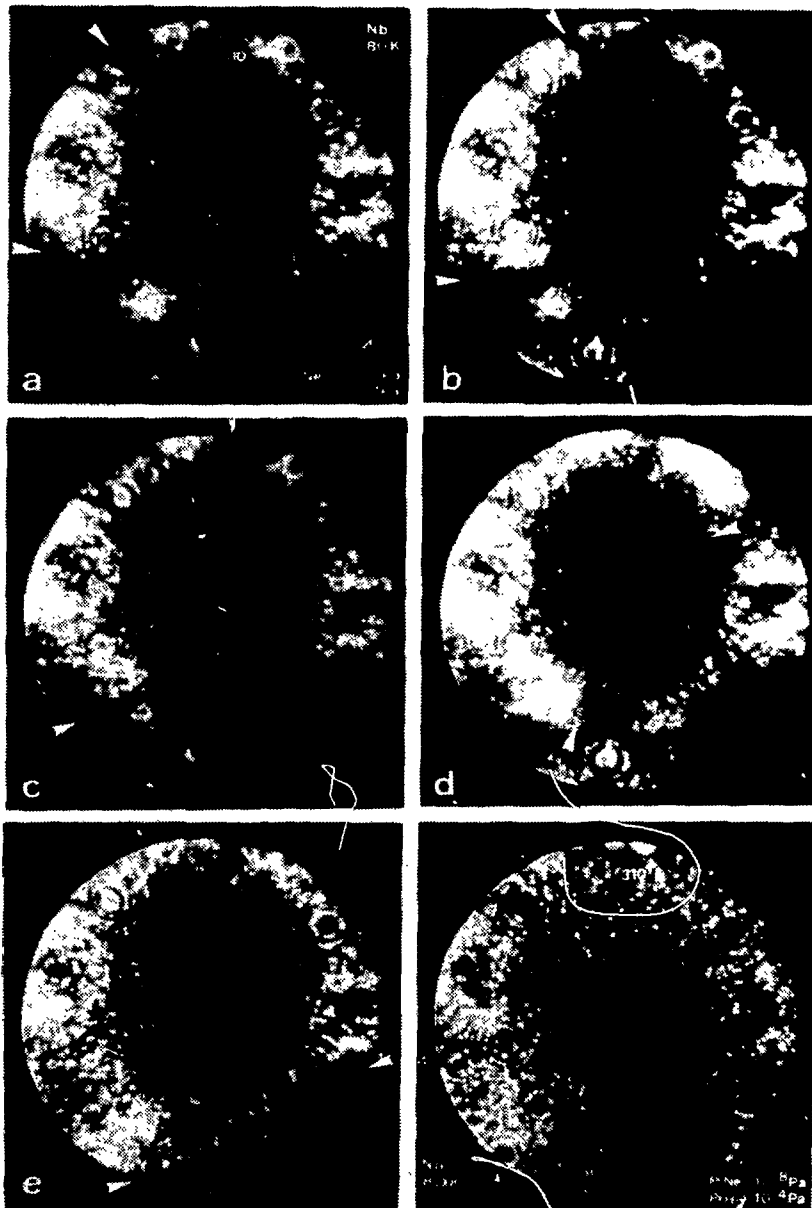


Fig.2.Nb imaged with Ne+1% H₂ at 80K.a-e) Extension of hydrogen promotion, f) Imaged with hydrogen

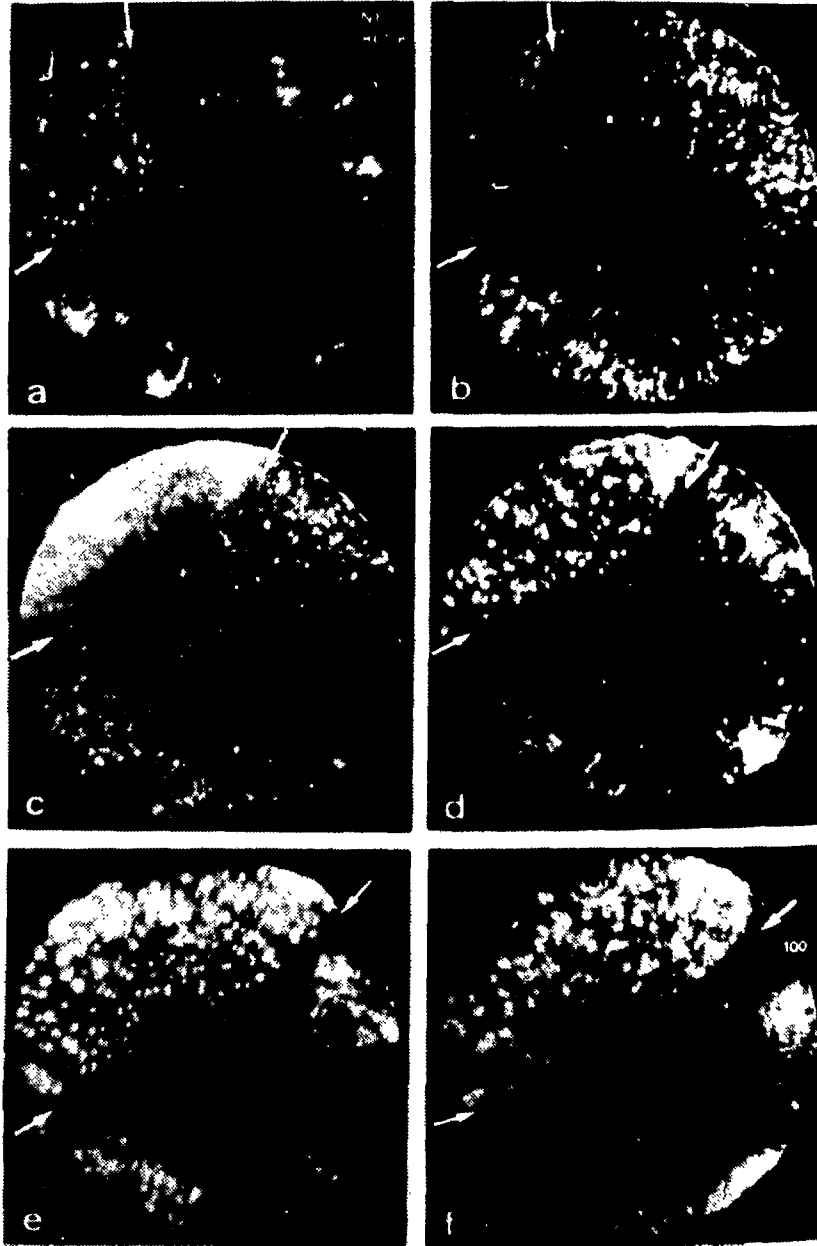


Fig.3. Nb imaged with Ne at 80K. a-f) Epitaxial growth of a layer withstanding field evaporation

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By heating a niobium tip in a residual gas containing small amounts of H_2O , N_2 , O_2 and CO at a total pressure of 10^{-6} Pa at $700^\circ C$ local surface changes occur as to be seen in Figure 3a using neon as imaging gas at a pressure of 10^{-2} Pa. Around the $12\bar{1}$ and $11\bar{1}$ poles at the upper left side a new layer has epitaxially grown up and extends as marked by the arrows if the applied voltage to the tip with an average tip radius of 35 nm is step wise increased from 9,5 kV to 11,5 kV whereby field adsorption is favoured (Fig.3b-d). This area withstands field evaporation at field strengths where the other parts of the clean niobium surface already highly field evaporate. In Fig.3e-f the tip has been turned down a little to get a better view till to the $10\bar{1}$ pole. The BIV for the clean and covered niobium differs by approximately 10%. It is to be assumed that the epitaxially grown up layer mainly consists of niobium nitride or carbonitride since thin oxide layers could be successfully field evaporated at sufficient high field strengths so that a clean niobium surface could be attained. It is hoped that the final decision concerning the composition of the grown up layer can be reached by laser pulse induced field desorption mass spectrometry which is, however, not accessible for us up to the present.

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