FIELD ION MICROSCOPIC INVESTIGATIONS OF NIOBIUM, TANTALUM AND PALLADIUM INTERACTIONS WITH REACTIVE GASES

E. Krautz, G. Haiml

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E. Krautz and G. Haiml

Institut für Festkörperphysik, Technische Universität Graz, A-8010 Graz, Austria

Résumé - Avec le microscope ionique à émission de champ, nous avons étudié les interactions des métaux Nb, Ta et Pd avec l'hydrogène, l'oxygène et l'azote et plus spécialement divers défauts cristallins directement observables avec la résolution atomique.

Abstract - With the field ion microscope we have studied the interactions of the metals Nb, Ta and Pd with hydrogen, oxygen and nitrogen especially different crystal defects directly visible in atomic resolution.

Adsorption and absorption of foreign atoms on and in transition metals can sensitively change the surface and the volume properties of these metals both in a wanted and also unwanted manner. While in alloys the solution of a second metal component is mostly used to improve certain physical properties the interactions of transition metals with reactive gases which occupy interstitial crystal sites cause there local polarizations, lattice deformations and dislocations. Higher concentrations of dissolved gas atoms in Nb, Ta and Pd affect precipitations and dislocations especially at lower temperatures when greater differences in lattice parameters and expansion coefficients occur in context with local phase changes what leads to unwished embrittlement and also increases the difficulties for FIM investigations. Numerous investigations of internal friction have proved that the interactions between various dislocations and dissolved light atoms are rather complex (1)-(6).

Whereas at the beginning the main aim was to prepare and investigate perfect single crystals and to destin their ideal properties one is now especially interested to investigate the different kinds of lattice defects. For such studies the transition metals of the 4. and 5. column of the periodic table of the elements are predestinated because they can absorb hydrogen, oxygen and nitrogen in remarkable high concentration partly in solid solution partly in internal precipitations with different composition and crystal structure (7). In this context the different diffusion coefficients of the light gases in different metals differ partly by many orders of magnitude (8)(9)(10). While hydrogen can diffuse in niobium and tantalum even at low temperatures by tunneling process the mobility of oxygen and nitrogen is there lower by more than 15 orders of magnitude. Oxygen becomes mobile in niobium but above 400 K and in tantalum above 600 K. Whereas hydrogen can be degassed by heating in UHV several hours above 1500 K to a high degree degassing of oxygen and nitrogen in UHV needs more than 2600 K for niobium and 2850 K for tantalum. Their diffusion coefficients decrease in the sequence Nb, Ta, Pd. The solution of hydrogen in these 3 metals is an exothermal reaction. Dissolved oxygen and nitrogen

atoms act as traps for hydrogen. Already a thin oxide surface layer can prevent hydrogen diffusion into and out of Nb samples (11). The temperature dependence of the hydrogen concentration obeys Sieverts equation at low hydrogen concentrations. Residual hydrogen can be removed by covering niobium with a thin coverage (0,2 µm) of palladium and heating the sample in an oxygen atmosphere of 200 mbar(12).

A remarkable stimulating effect we have found if very high electric fields were applied during gas-metal reactions. While physisorbed hydrogen, oxygen and nitrogen on metal surfaces at low temperatures usually can easily be field desorbed this becomes more difficult if the reaction has taken place at higher fieldstrengths because a stronger field induced binding is established especially for interactions of Nb and Ta with reactive gases penetrating deeper into the bulk yet at lower temperature in the presence of sufficient high electric fields than needed in the absence of high fields. This was detected during field evaporation and profile measurements with the FIM atom-probe (13)(14).

Results and Discussion

To study the initial stages of the reaction of niobium and tantalum with oxygen and nitrogen the tips were heated few minutes at 700°C in a residual gas at a pressure of 10^{-6} Pa mainly containing hydrogen, water vapour and a small content of carbonmonoxid which together led to a surface oxidation. The thin oxide layer could easily be field evaporated since the field evaporation field strength therefore was approximately 10 % smaller than that for the corresponding clean metal surface.

If under similar conditions the heat treatment was applied in a nitrogen atmosphere it was more difficult to remove the nitride layer by field evaporation because the necessary field evaporation fieldstrength was nearly equal to that for the metal itself. When in addition carbonhydrides were present which allowed the formation of dense carbonnitride or even carbide coverages the corresponding field evaporation fieldstrength exceeded the values for both metals. Cleaning of the surface by fieldevaporation was then hindered.

The initial stages of reaction for instance of niobium with oxygen and nitrogen shows characteristic differences. While the reaction with nitrogen spreads rather homogeneously over the whole niobium surface the oxidation of niobium begins in low indexed areas insularly.

In all three metals Nb, Ta and Pd dissolved hydrogen, oxygen and nitrogen produce many lattice defects as is shown in the following figures.

For the demonstration of the influence of dissolved reactive gases in case of tantalum two wires with different mechanical and electrical properties were selected. The preparation of the tips has been performed under exact same conditions by etching in a dilute melt of KOH facilitated by an ac voltage less than 1 V. Nickel was used as crusible material.

In Fig.1 the two upper FIM-pictures a and b belong to a tantalum wire Ta I with a good ductility and a low residual resistance whereas the FIM-pictures c and d concern the wire Ta II which was less ductile and had a higher residual resistance. Different imaging gases were applied as noted in the caption. Best atomic resolution has been reached with the gas mixture He+Ne at 3.10^{-2} Pa as to be seen in Fig.1a for Ta I.

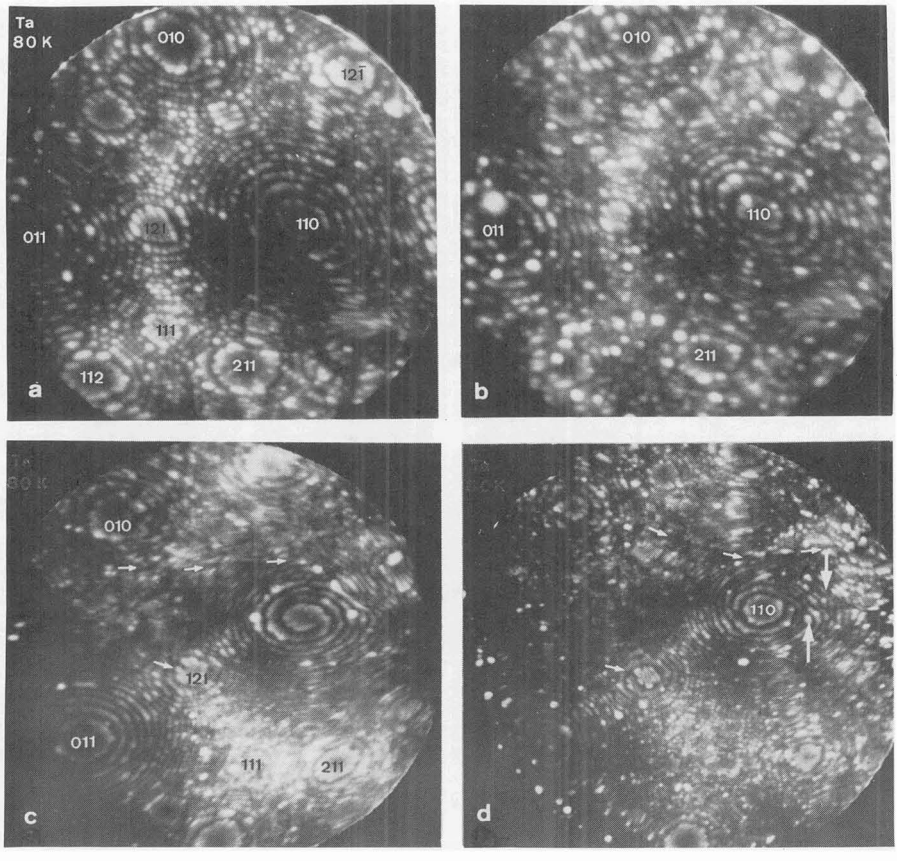

Fig. 1 - FIM-pictures of Ta imaged at 80 K. Imaging gas: a) helium + neon, b) hydrogen c) and d) neon at a pressure of 3.10^{-2} Pa. a) and b) Ta I with low, c) and d) Ta II with higher concentration of dissolved reactive gases.

Less atomic resolution was obtained if hydrogen was used as imaging gas as in Fig. 1b because of surface reaction and adsorption processes. The FIM-picture of Fig. 1c shows many lattice defects and dislocations marked by arrows. We studied in more detail the dislocations caused by light gas absorption especially at the <121> and <110> poles during field evaporation of 150 layers (110) as finally shown in Fig. 1d. Numerous new and disappearing dislocations were observed. Whereas the dislocation spiral on the (121) remained unchanged with a Burgers vector a/2 [$\bar{1}$11] continuous changes of the dislocation spiral at (110) were noticed. In Fig. 1d two opposite spirals marked by arrows are of special interest. The bending net plane rings indicate that in this case partial dislocations are present which give rise of a stacking fault. Similar properties have been observed also for niobium with and without dissolved hydrogen, oxygen and nitrogen and with and without cold work treatments.

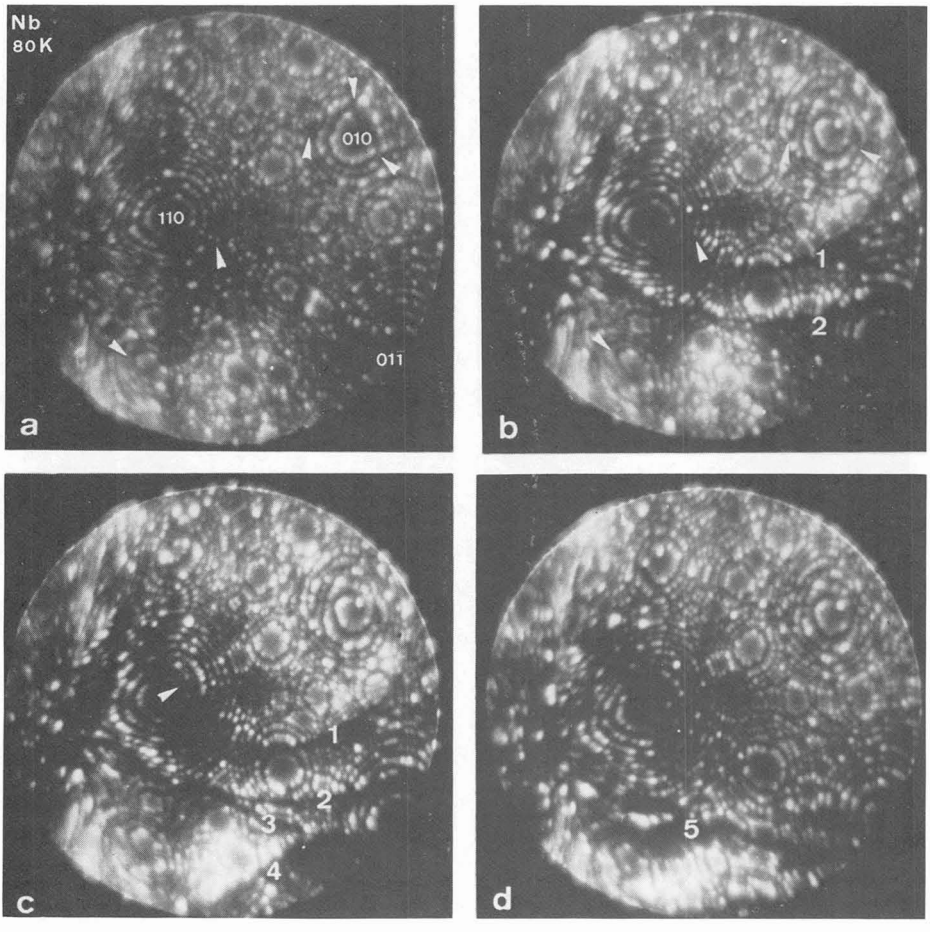

Fig. 2 - FIM-pictures of Nb with dislocations and slip steps 1,2,3,4,5 imaged with neon at 3.10^{-2} Pa and 80 K before rupture of the tip. Time intervals 2 seconds.

Interesting dynamical processes could be observed with niobium tips etched in a melt of KOH and $NaNO_2$ and electropolished with ac voltages between 0,5 and 1,0 V when hydrogen and oxygen had been dissolved in the tips. If such Nb tips at high fields are warmed to 50°C in UHV and then imaged with neon at 3.10^{-2} Pa during cooling down the sample one observes sudden displacements of larger surface areas by fits and starts. To prevent a rupture of the tip the fieldstrength has been diminished by nearly 10 %. It was then possible to image the appearance of slip steps within time intervals of 2 seconds.

Fig.2a shows the FIM picture of a niobium tip with dissolved reactive gas imaged with neon at 3.10^{-2} Pa at 80 K with a larger disturbed area on the left side after rupture of a lamella and many dislocations on the right side of the picture several marked by arrows. The Fig.2 b,c, d show the successive appearence of slip steps 1,2,3,4,5 within 6 sec.

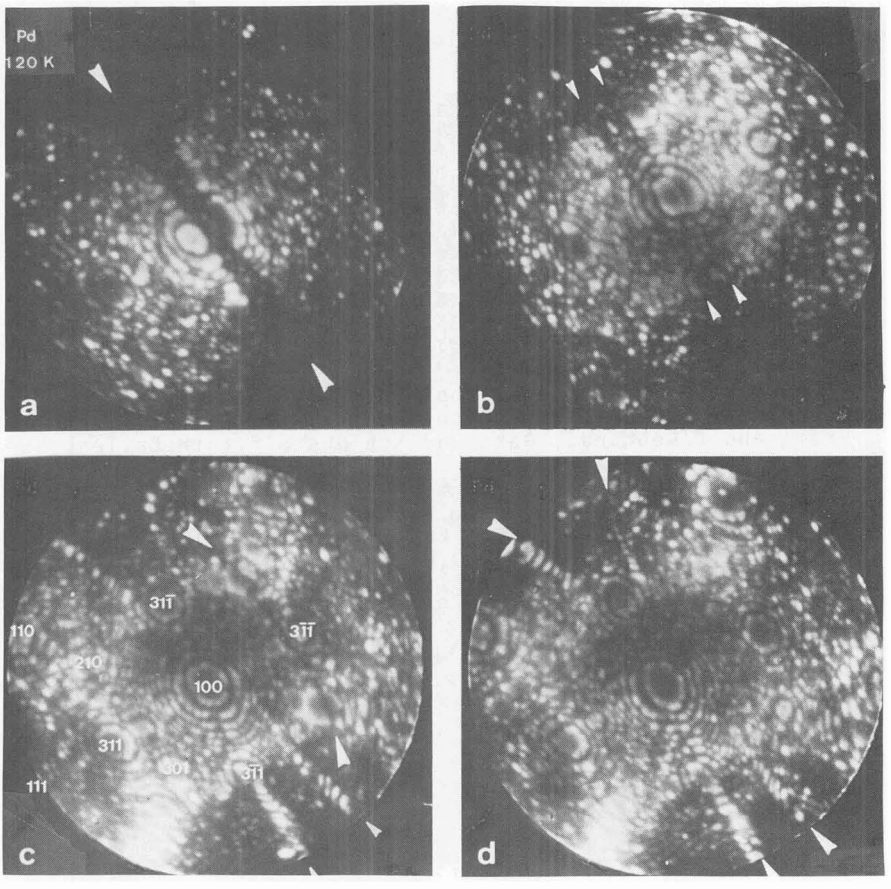

Fig. 3 - FIM-pictures of Pd with dislocation and stacking faults with decoration imaged with hydrogen at 10^{-3} Pa and 120 K.

The dislocation dipol to be seen on the (010) plane in Fig.2b extends after field evaporation of one layer over two planes as can be recognized in Fig.2c. The slip steps 1 and 2 allow to determine the Burgers vector a/2 [1$\bar{1}$1] belonging to this dislocation. The first four slip steps of Fig.2b and c disappeared rapidly by field evaporation before slip step 5 in Fig.2d appeared.

Fig.3 shows FIM-pictures of a Pd tip in [100] orientation with a tip radius of 27 nm imaged with hydrogen at 120 K. Various lattice defects can well be recognized. The broad dark stripe through the central (100) plane in Fig.3a and b marked by arrows is limited by slip steps which are originated by partial dislocations. This is proved by the stepped spiral to be seen on the (100) plane in Fig.3b after the field evaporation of 3 layers (100). Further field evaporation of 3 layers (100) led to the Fig.3c. The narrow dark trace between the larger arrows in Fig.3c indicates a perfect dislocation with a Burgers vector a/2 [100]. The slip plane of this dislocation is a (111) plane. This dislocation disapppeared yet after field evaporation of only one (100) layer.

The bright decorated trace is related to a stacking fault produced by partial dislocations. The splitting of the bright decorated traces at the rim supports the conclusion that the relating slip planes are (111) planes. In this case the dislocations are partial dislocations of type a/6 [112].

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