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Influence of steel on the mechanical stress development during hydrogen-loading of ultrathin Nb-films

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ABSTRACT

Thin films attached on rigid substrates can develop ultra-high compressive stresses upon hydrogen-loading. These high stresses can be released by dislocation-formation or delamination. For niobium thin films dislocation-formation was observed for films thicker than 6 nm upon hydrogen-loading up to 1 H/Nb. By alloying niobium with steel the critical film thickness for dislocation formation can be increased to at least 37 nm. TEM and EELS studies on the film's microstructure and elemental distribution show Fe-enriched regions being present at grain boundaries. This refines the hydrogen-absorbing Nb grain sizes thereby hardening the material.

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Introduction

Hydrogen (H) absorption in interstitial lattice sites of a metal film leads to in-plane stresses, if the metal film is bound to a rigid substrate [1,2]. For low hydrogen-concentrations the hydrogen induced stress in the film increases linearly, whereas for higher concentrations and above the material dependent 'yield stress', the stress build-up is often reduced e.g. by the creation of dislocations [3]. These dislocations are of different origin. Because of the initial misfit between the film (f) and the substrate (s), misfit-dislocations are expected to form at the film/substrate (f/s) interface [4]. For niobium (Nb) films adhered to sapphire (Al_2O_3) substrate, f/s-misfit-dislocations are reported to appear for films thicker than

6 nm, in the initial state [5]. Hydrogen absorption in the Nb-film results in Nb-lattice expansion and, thus, in an increase of the misfit between the film and the substrate. Hydrogen uptake of up to 1 H-atom per Nb-atom, given in H/Nb, commonly yields to new hydrogen induced f/s-dislocations [3].

The critical hydrogen concentration, above which these new f/s-dislocations are formed, depends on the film thickness. For a hydrogen uptake of up to 1 H/Nb, Matthews and Blakeslee's formalism suggest, that f/s-dislocations occur at film thicknesses of 7.2 nm and above [5–8]. Below this film thickness, no hydrogen-induced f/s-dislocations are expected, even upon loading of up to 1 H/Nb.

Caused by the misfit between the Nb-hydride (h) and the Nb-matrix (m) a second type of dislocations can occur in the concentration range of the two-phase field of the Nb–H phase

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diagram. During loading with hydrogen, hydrides form and expand in volume density. h/m-dislocations are reported to appear for Nb-films with a thickness above 26 nm, as predicted theoretically [9]. The experimentally observed thickness of 38 nm is slightly larger [10]. When the hydrides are of cylindrical shape, these h/m dislocations may appear as dislocation rings.

Hamm et al. recently showed that the absence of stress release can result in ultra-high mechanical stress [3]. This was confirmed for 6 nm Nb-films yielding compressive stresses of -10 GPa (± 1 GPa) for hydrogen concentrations of $c_H = 1$ H/Nb during the first loading cycle, and for slightly thicker films of up to 10 nm, after the first loading cycle [3]. For these films, dislocation formation led to a partial release of compressive stress during the first loading cycle and to a residual tensile stress after the first loading cycle. For even thicker films, dislocation formation was reported also in the second loading cycle [11] resulting in reduced maximum compressive stress.

In bulk material, dislocation formation and propagation is influenced by solvents ('solution hardening') and also by the presence of precipitates ('precipitate hardening'), both hardening the material. A similar influence of solvents on the material hardness is expected for thin films. According to the binary bulk-phase diagram, iron (Fe) alloying with Nb results in the formation of NbFe intermetallic phase, above a solid solution limit of 1 at% Fe [12]. For a mean iron content of 12 at % Fe, the lever rule suggests 22% of intermetallic NbFe phase and of 78% solid solution (Nb). Assuming the Fe–Nb phase diagram of the thin film to resemble that of the bulk system, about 22% volume fraction of NbFe on the total volume are expected to influence the dislocation behaviour.

Fe-addition commonly increases the hydride formation chemical potential, as described in Ref. [13] (Section 3.1) and [14]. Thus, in case of the intermetallic phase FeNb, only very limited hydrogen absorption is expected to appear, under ambient conditions.

In this presentation we study the effect of an addition of Fe on the film microstructure, on the stress development and dislocation appearance in Nb thin films, by mechanical stress measurements and cross-sectional transmission electron microscopy (TEM).

Experimental details

Nb thin films and Nb-steel films were cathode beam sputtered on polished sapphire Al_2O_3 substrates ($<0.1^\circ$ miscut, Crystec). The out-of-plane-orientation of the substrate is (1120) and [0001] in-plane (c-plane orientation). This orientation allows for an epitaxial Nb film growth in a (110) out-of-plane direction and [111]-in-plane relation to the c-plane orientation of the substrate [15,16]. This relation mainly remains for the Nb grains in the Nb-steel films. The substrate size was (7 mm \times 30 mm \times 0.1 mm) where the c-axis of the Al_2O_3 crystal is aligned along the long edge.

The films were deposited in an ultra high vacuum (UHV) apparatus (BESTEC) with a background pressure of 10^{-8} Pa. The sputtering pressure was 4×10^{-2} Pa of Argon (99.9999% purity). Growth rates were 0.32 nm/min for niobium (99.99% purity) and 0.5 nm/min for palladium (99.95% purity). The

steel-content of 20 at% was added by co-sputtering 303 stainless steel (70 at% Fe, 18 at% Cr, 9 at% Ni, and 3 at% total rest components) The majority component of this steel is Fe. A small amount of Cr and Ni is also present in the Nb-steel films. According to the binary phase diagrams, Cr as well as Ni form intermetallic compounds with Nb. Thus, these elements result in an increase of the hydride formation chemical potential like the Fe does. Nb and steel were deposited at a substrate-temperature between $750^\circ C$ and $800^\circ C$, the palladium capping layer was added at ambient temperature. We note that also the Pd contains steel. Different Nb and steel-Nb film thicknesses were chosen ranging from 3 nm to 40 nm. All Pd layers were about 6 nm thick.

The epitaxial relation of the Nb-steel film was confirmed by electron back scatter diffraction (EBSD) and XRD. The content of Fe, Cr, and Ni in the films was confirmed by electron-microprobe studies (WDS) and energy dispersive X-Ray spectroscopy.

The films were electrochemically loaded with hydrogen in a phosphorous electrolyte. The electrolyte consists of a mixture of two parts of 85% glycerine and one part of 85% phosphoric acid [17]. Faraday's Law allows calculating the introduced hydrogen concentration in dependence of the flown electrical charge Q:

$$\Delta c_H = \frac{\Delta n_H}{n_M} = \frac{Q}{F} \frac{V_m}{V_s},$$

with V_m representing the molar Volume of the film, V_s the total volume of the film and F being Faraday's constant. Simultaneously, the electromotive force (EMF) was recorded in comparison to an Ag/AgCl-electrode (SCHOTT Instruments GmbH).

Stepwise and continuous hydrogen-loading were performed, resulting in no apparent difference in substrate curvature and EMF. Hence, the majority of loading-cycles were performed in a continuous manner. All samples were loaded from zero to one H/Nb, assuming pure Nb films for the calculation of electrical charge Q. Each sample endured several loading cycles.

During hydrogen absorption, Nb expands linearly by a factor of $\alpha_H = 0.058$. A thin film of Nb, rigidly clamped onto its substrate, results in a larger strain in out-of-plane direction with $\alpha_H = 0.137$, according to linear elastic theory. In in-plane direction the expansion factor is, in contrast to this, zero. The in-plane stress can be computed, using the bulk Nb elastic constants, $C_{11} = 245.6$ GPa, $C_{12} = 138.7$ GPa and $C_{44} = 29.3$ GPa at 300 K [11], to be $\sigma_{[111]} = 9.1$ GPa $\times c_H$ [3]. The stress value of the Nb-[111]-direction is applicable for all regarded films as they were all tested in that orientation.

As FeNb and the other intermetallic phases only absorb tiny amounts of hydrogen at the chosen conditions, any stress increasing effects from these phases can be neglected. However, these phases have to be considered as the measured stress is the net result.

The in-plane mechanical stress in the films was measured by substrate curvature measurement [3,18]. The stress is calculated from the curvature using Stoney's equation [19–21]. Due to the hexagonal symmetry some adaptations [22] of the formula lead to the following equation:

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