# KINETIC AND CRYSTALLOGRAPHIC ASPECTS OF NITRIDING OF METALS IN A LOW PRESSURE NITROGEN PLASMA: NIOBIUM AND MOLYBDENUM

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## EXTENDED ABSTRACT

The kinetics of nitriding of metals has been studied by means of in situ thermogravimetry using a quartz spring microbalance [1]. It has been found that the weight increase of the sample due to the nitriding can be approximated by a simple $\sqrt{t}$-dependence only within a limited time interval $\Delta t$. For time periods less than $\sim 2$ hours these deviations are attributed to the variation of the sample temperature which appears to be due to changes of the surface properties upon nitriding. Deviations which appear during long term nitriding are attributed to changes of the diffusion rates by a sequential occurrence of various phases, i.e. α-Me solution, $Me_2N$- and MeN phases. Measured nitrogen concentration depth profiles support this interpretation [1, 2].

From Arrhenius plots of the reaction rates the following rate constants for the formation of the $Me_2N$ phases have been found:

$Nb_2N$: $k = 3 \times 10^4 \exp - (24'260 \pm 350)/RT$

$Mo_2N$: $k = 1.4 \times 10^7 \exp - (31'000 \pm 500)/RT$

($E_{act}$ in cal/mole, k in $\mu g^2 \cdot cm^{-4} s^{-1}$)

Whereas there is no apparent effect of the plasma on the rate of nitriding of niobium as compared with molecular nitrogen (1 at.), molybdenum is nitrided by orders of magnitude faster in a nitrogen plasma at ~1 torr as compared with molecular nitrogen at 1 at.

Along with the kinetic measurements crystallographic and morphology studies of the nitrides formed have been done as well. In case of niobium nitride a new pseudomorphic orthorhombic phase β-$Nb_2N$ has been proposed. This is metastable

and it exists only because of the epitaxially induced forces in the nitride layer as long as it remains in tight contact with the metal.

A long term nitriding of thin molybdenum foils (5 μm) yield the well known hexagonal δ-MoN phase which is subsequently transformed into a new hexagonal δ'-MoN one of a lower density, as determined by means of x-ray diffraction. This transformation is accompanied by a remarkable increase of the nitriding rate almost up to the theoretically expected MoN stoichiometry of the whole foil.

REFERENCES

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[2] C.Braganza, S.Veprek, E.Wirz, H.Stüssi and M.Textor, these proceedings: Topical Meeting on Interaction of Low Pressure Plasmas with Solid Surfaces.