Reversed Kinetic Isotope Effect during Penetration of Cathodic Hydrogen/Deuterium into NiCu30 Alloy

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The cathodic charging with H/D of a NiCu alloy containing 30 At.-% Cu followed by magnetic measurements indicates that D penetrates faster into the alloy than H.

Magnetic investigations into the cathodic absorption of hydrogen/deuterium in bulk nickel didn't show any remarkable kinetic isotope dependence[1]. But the maximal penetration depth of the hydride/deuteride phase was smaller during the cathodic absorption of deuterium than of hydrogen[2, 1]. In both cases selendioxid was used as catalytic promoter. Hereby however it is difficult to analyse the results of measurements as selen is deposited during the electrochemical process on the surface of the sample.

In contrast to pure Ni the annealed alloy of Ni with 30 At.-% Cu has the advantage of absorbing hydrogen without any catalytic promoter[3] so that no influence of a promoter may interfere.

Because of this finding we began to extend our studies of isotope effects on the alloy NiCu30. In the experiment we could follow the absorption of the hydrogen isotopes by the magnetic method described earlier[1, 4], because non-magnetic NiCu-hydride resp.-deuteride is formed. (The decomposition process of these systems during which ferromagnetic NiCu30 is formed back is more complicated, c. f.[1, 5]). – For the experiment 20 μm thick foils of NiCu30 were used, which had been heat treated for three hours at 550 °C; they were charged cathodically at room temperature at a current density of 20 mA/cm^2 in 0.5 n H_2SO_4 resp. D_2SO_4 up to an volumetricly controlled atomic ratio of at least 0.4 H(D)/alloy.

The measurements show that the magnetic flux diminishes more rapidly on samples charged with deuterium than on those charged with hydrogen. From this can be inferred that deuterium penetrates faster into the alloy. When the cathodic charging of a sample is repeated as well as in case of alternating the charging of a sample with hydrogen resp. deuterium this result is preserved.

Repeated charging leads to an increase of the penetration velocity for both isotopes and to the decrease of lags in the beginning of the reaction; this happens because of the 'training' of the material, which is well known from the Ni-H/D-system (cf.[2]).

In Fig. 1 the instance of a (third) cathodic charging of NiCu30 with hydrogen/deuterium is shown. From the logarithmic diagram a ratio of the velocity constants of $k_D/k_H = 1.5 \pm 0.2$ can be gathered. Similar ratios were found with all experiments.

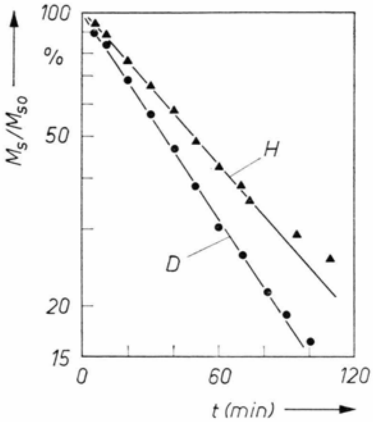

Fig. 1. Relative saturation magnetization M_s/M_{so} of a NiCu30 foil versus time of cathodic absorption of hydrogen (H) resp. deuterium (D) at 21,5 °C. M_{so} = saturation magnetization before the absorption.

In contrast to the classic rate theory[6, 7] according to which the light isotope diffuses more quickly than the heavier one the quantum-statistic theory of Ebisuzaki et al.[8] gives the ratio $D_D/D_H = 1.25$ for Ni. As our result shows the same tendency the possibility is offered to interpret the isotope effect investigated by us not merely as a phase boundary effect.

A reversed isotope dependence for hydrogen diffusion in metals was first observed by Wicke et al. in gasvolumetric[9] and electrochemical[10] investigations on Pd and Pd alloys. For the formation of the hydride-resp. deuteridephase of PdAg25 for instance the ratio of $D_D/D_H = 1.35$ was found at 25 °C[10]. Qualitatively these results were confirmed by diffusion measurements, based on the Gorsky effect[11].

As to the question in which degree the isotope effect observed is really caused by the different velocity of bulk diffusion of the hydrogen isotopes in the alloy pertinent investigations on foils of different thickness and at different temperatures are being undertaken.

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