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Accelerated Formation Kinetics of Nickel Hydride in a Planar Ni Foil

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Kinetics of nickel hydride formation was investigated during the electrolytic charging and the parabolic law dependence was clearly stated [1]. Recently, during the investigation of the penetration depth of nickel hydride in planar foils as a function of hydrogen pressure [2], an unexpected acceleration of the formation kinetics was observed in the final period of formation before the advancing hydride fronts met in the center of the Ni-foil investigated. Fig. 1 presents an example of such behavior.

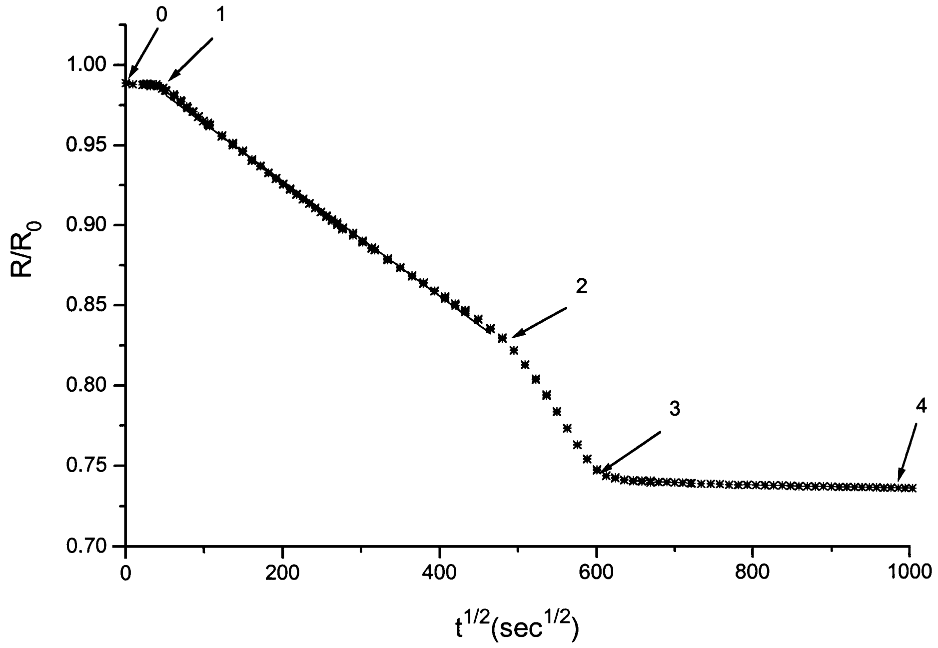

Figure 1. The relative electrical resistance (the ratio of the electrical resistance of a 13 × 1.5 mm × 50μm Ni foil at the time indicated to the initial electrical resistance of the same (pure) foil as a function of square root of exposition time to 14.05 kbar of gaseous hydrogen at 25°C. The electrical resistance was determined "in situ" by the four pole technique. For details see [2]. 0–1 induction period, 1–2 normal nickel hydride formation, 2–3 "accelerated" nickel hydride formation, 3–4 complete penetration of the nickel foil by the hydride phase.

As a function of time the above figure can be divided into four consecutive parts: From the starting point up to about 30 min (0→1) an induction period is clearly noticed, caused by the activation of the surface and the saturation of the nickel foil by hydrogen up to the saturation limit of the α-phase (solution of hydrogen in nickel up to about 10^{-3} in atomic ratio H/Ni). This induction period terminates around point 1 in Fig. 1. In many cases a slight increase of R/R_0 is noticed, caused by the growth of scattering centres concentration, formed by the hydrogen particles dissolved. The induction period is followed by a long (about 54 hours) linear part of the relative resistance as a function of square root of time, representing the formation of nickel hydride penetrating from both sides of the foil (from 1 to 2 in Fig. 1). The linearity presented on this part in Fig. 1 expresses the parabolic law, well known in phase transitions in solids. Assuming proportionality between the change of the relative electrical resistance and the penetration depth of the hydride layer, we estimate that the first linear part of the R/R_0 *versus* to $t^{1/2}$ curve between 1 and 2 corresponds to a penetration depth (from each surface of the foil) of about 17 μ. Between points 2 and 3 in Fig. 1, a more rapid formation of nickel hydride follows, taking about 3.7 hours and corresponding to each side penetration depth of about 8 μ. On the average, the time period between 1 and 2 represents a formation rate of nickel hydride of about 0.3 μ per hour, whereby the „accelerated" period between 2 and 3 in Fig. 1 corresponds to the formation rate of about 2.1 μ per hour – thus, a 7 times higher rate compared to the previous period. In other words, the approach to one another of the nickel hydride fronts, before they are coming to a contact (around point 3), thus, reducing the rest of unpenetrated nickel layer, is taking place in a much higher rate!

The crucial question, which now arises, is: Why is the final rate of the approach of both hydride fronts to one-another so much higher than the previous hydride penetration? To explain this behavior it seems unavoidable to consider the stress fields created by the hydride formation. The molar volume of stoichiometric nickel hydride is about 9% larger than that of pure nickel. This volume increase creates in the neighboring nickel layers a high expanding and deeper a compressive stress, which has to be overcome by the advancing hydride front. Due to the non-local character, the stress fields from opposite hydride fronts meet together in the still unpenetrated nickel layer, thus, an effective reduction of the previous obstacle for the further hydride penetration is to be expected. In other words, the meeting of both penetrating fronts is realized under more favorable conditions than the previous penetration. Therefore, the transition of the final nickel layer is, in respect to the necessary expansion of the nickel lattice, required for the hydride formation, favoured by the approach of both hydride fronts. Here the question arises, why the above acceleration occurs at the distance of approaching hydride fronts mentioned above. Anyway, the non-local character of the stresses, accompanying the phase transition considered, is clearly demonstrated.

One can find a corresponding model in macroscopic mechanics of an elastic medium, exhibiting a similar behavior. Imagine a hard nail, penetrating an elastic medium. Applying a constant stationary force from outside on the nail, one expects that the penetration depth of the nail will be determined by the equilibration of the force applied on the nail from outside and the resistance of the medium penetrated. An increase of the external force will cause an increase of the penetration depth of the nail involved. If an elastic plate will be penetrated by two nails from exact two opposite sides, the final penetration period, before tauching one – another of both nails, will be accompanied by an acceleration, because the stress fields created by both nails, being non-local, will facilitate the final penetration just before meeting of both nails. The role of nails play in this case the penetrating hydrogen particles, which, like the nails, create a stress field. Meeting of the penetrating fronts (the hydride fronts or the nails) is expected to be facilitated in the final period, before both fronts reduce the final part of the non-penetrated medium, being a consequence of the non-local character of the stresses created.

Let us remark that the total penetration of the Ni-foil considered is accompanied by the reduction of the initial (pure Ni) electrical resistance by about 30%. This value is found as being characteristic for a complete nickel hydride penetration and was used above for the estimation of the penetration depth of the phase created.

The time course presented in Fig. 1 is not a unique event. It was observed also in cases where different thicknesses of the foils and different hydrogen pressures were applied, leading to a complete penetration by the hydride phase. An extended analysis of the nickel hydride formation kinetics will be published later.

It is to be expected that a similar „acceleration" of the phase transition kinetics, when the phase fronts are approaching to one – another from opposite sites of a planar system, should be observed in similar phase transitions to hydride formation, considered above. The magnitude of this acceleration will surely depend on the stress field created during the phase transition considered, what means that smaller volume differences between the phases considered will cause a corresponding smaller acceleration of the final formation period, due to smaller accompanying stress fields.

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