Investigation of the hydrogen neutrals in a discharge source used for production of metal hydrides

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Abstract. The paper discusses the possible mechanisms for production of metal hydrides (MH) in a DC discharge source. The results of different experiments suggest that the molecules are sputtered directly from the surface of the cathode, where they are formed after adsorption of atomic hydrogen. This hypothesis allows one to understand the operation of the source studied and to optimize its working conditions.

1. Introduction

The high-resolution studies of transition MH (e.g. NiH, FeH, CrH) is motivated mainly by their importance in astrophysics [1, 2]. These molecules have a significant permanent magnetic moment and their presence in the spectra of cold stars allows for the assessment of magnetic fields by the Zeeman splitting and/or broadening. The interpretation of the astronomical observations needs reliable data on the electronic structure of the molecules and on the Landé factors, which can be obtained by high-resolution laboratory measurements [3, 4]. Along with the analysis of a complicated electronic structure, a challenge for the laboratory studies is the effective production of MH. Several sources can be found in the literature, most of them utilizing gas discharges, e.g. [2, 5, 6]. Their performance is comparable, each of them having advantages and disadvantages regarding the densities of the molecules, absorption length, suitability to perform measurements in magnetic fields etc. Some of the sources work effectively in pure hydrogen [5], others, in Ar:H\textsubscript{2} mixtures [2, 6], which indicates different mechanisms for production of MH. This paper presents a study on the performance of the recently reported discharge tube with coaxial geometry [7] in order to shed more light on the pathways for production of MH. Understanding these processes is important for finding the optimal working conditions and, generally, for future construction of sources for MH.

The experimental results on NiH, reported in [7], were obtained by applying laser absorption spectroscopy in pure H\textsubscript{2}. It was established that during the operation of the tube, the molecular signal decreases, presumably due to the heating of the cathode. Therefore it was suggested that the formation of NiH is connected with the adsorbed hydrogen on the cathode surface. In this contribution we study this hypothesis and give further evidence that supports it.

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2. Operation of the NiH source
A detailed description of the coaxial discharge tube is given in [7]. The cathode consists of eight separate nickel rings with an inner diameter of 65.5 mm, forming a cylinder with a total length of 250 mm. The anode is formed by six stainless steel rods (1 mm in diameter, 300 mm long) laid equidistantly on a cylindrical surface (coaxial with the cathode) with a diameter of 31 mm. The electrodes are mounted in a glass tube equipped with separate electrical feedthroughs for each of them. The discharge is investigated at gas pressure $p = 200$, 500 and 1600 mTorr and applied DC current $I = (20–200)$ mA. The voltage drop between the cathode and the anode amounts to (350–650) V.

The pressure in the tube changes significantly in a regime of operation without a gas flow (figure 1(a)). After the ignition of the discharge, the pressure initially drops, than it gradually increases and the higher the current the sooner it happens. Depending on the initial conditions ($p$, $I$), within 5–6 minutes the gas pressure may triple. The possible reason for this behavior could be the competition between the adsorption of hydrogen on the cathode surface and its desorption. At the present range of gas pressures $p = (200–1600)$ mTorr, and when the discharge is turned off, the adsorption rate is bellow the sensitivity of our detectors (0.1 mTorr/s) for cathode temperatures in the estimated range of 20–70 °C. This means that the adsorption in the current study is mainly due to hydrogen atoms or hydrogen ions – particles produced in the discharge. On reaching the cathode, the hydrogen atoms may be reflected back as atoms or molecules or they may stick to the surface, the latter process contributing to the adsorption. In contrast with the atoms, the ions are accelerated in the constant electric field and they reach the cathode with a significant energy – tens to hundreds of eV depending on the applied voltage and the collision rates with other particles. At the cathode, the ions may be neutralized and back reflected as neutral atoms or they may sputter particles from the cathode, including H, H$_2$ [8, 9] and NiH. The later process will influence the desorption. The ions may contribute also to the adsorption if they stick to the cathode. Most of the processes associated with ions lead to energy transfer to the cathode and its heating, which in turn reflects on the probabilities of some of these reactions.

At low currents, respectively low voltages, the processes of adsorption prevail over the desorption, resulting in a pressure reduction (see figure 1(a)). The ions density is low and the cathode remains at a low temperature. At higher currents, the density and the energy of the ions also grow, which leads to heating and intensive sputtering of particles from the cathode. These processes assist the desorption of the hydrogen back to the volume, raising the gas pressure. The interplay between adsorption and desorption in time can be traced out in figure 1(b), where the difference between the desorption and the adsorption rate (called here gassing rate) is illustrated. Before the measurement, the cathode is “filled” with hydrogen by running the discharge for few minutes at a low current ($I = 20$ mA) to prevent heating. When the current is set to 200 mA, the temperature of the cathode rises and, initially, the rate grows because of the increasing desorption. After about 60 seconds, however, a substantial amount of hydrogen is sputtered from

\[
\begin{align*}
p \text{ [mTorr]} & \quad t \text{ [s]} \\
0 & \quad 0 \quad 10 \quad 20 \quad 30 \quad 40 \quad 50 \quad 60 \\
400 & \quad 450 \quad 500 \quad 550 \quad 600 \\
\hline
I = 20 \text{ mA} & \quad I = 50 \text{ mA} & \quad I = 100 \text{ mA} & \quad I = 200 \text{ mA}
\end{align*}
\]

\[
\begin{align*}
\text{Gassing rate [mTorr/s]} & \quad t \text{ [s]} \\
30 & \quad 60 \quad 90 \quad 120 \quad 150 \quad 180 \\
2.0 & \quad 2.5 \quad 3.0 \quad 3.5 \quad 4.0 \quad 4.5 \quad 5.0
\end{align*}
\]

\textbf{Figure 1.} Time dependence of the pressure in the tube at different applied currents (a). Time dependence of the gassing rate at $p = 500$ mTorr and $I = 200$ mA (b).
the cathode and the desorption rate starts to decrease. Without “filling” the cathode, the gassing rate decreases immediately after the ignition of the discharge.

It is well known that hydrogen sticks to the metal cathode, forming a molecular bound with atoms from the crystal structure [8, 10]. Therefore, the process of sputtering of NiH molecules seems to be plausible – it was considered as the main process for formation of NiH in the current source [7]. The experimental observations in [7] show that (i) the density of the molecules decreases with the time, (ii) increases with the current and (iii) has an optimum at about \( p = (300–500) \) mTorr. The time dependence (i) of the molecular signal can be explained with the gradual heating of the cathode, which increases the hydrogen desorption from the surface and leads eventually to a reduction of the adsorbed hydrogen, i.e. reaching conditions for sputtering of less NiH molecules. At a given gas pressure (ii), the increase of the current results in higher density and energy of the ions, higher sputtering rates and, consequently, to an increase of the NiH signal. The main reasons for the pressure dependence (iii) of the molecular signal at a fixed current could be explained as follows. The lower pressures presume ions with higher energies, resulting in significant sputtering of NiH. This happens for a very short time, because of the fast heating of the cathode and the desorption of the hydrogen. At higher pressures, the density of ions is higher but their energies are lower and provide lower sputtering rates.

3. Spectroscopic observations

The spectroscopic observations are carried out at a current \( I = 200 \) mA and at stable gas pressures \( p = 200, 500 \) and 1600 mTorr, ensured by the flow regime of operation (gas flow rates between 10 and 40 sccm). The light emitted from the discharge along the axis of the cathode, i.e. perpendicularly to the direction of the electric field, is delivered simultaneously to a spectrometer for detection of emission spectra (Hamamatsu TM-VIS/NIR, 320–1000 nm) and to an interferometric system for analyzing the profile of the \( \text{H}_\alpha \) spectral line. Detailed description of profile investigation, including the experimental apparatus, can be found in [11]. Briefly, the light collected from the discharge by a light guide is directed to a Fabry-Pérot interferometer through a band pass interference filter for separation of the \( \text{H}_\alpha \) line. The corresponding interferogram is recorded with a digital camera and analyzed in order to extract the profile of the spectral line. During the discharge operation (3–5 minutes) a series of several spectroscopic measurements (emission spectrum and interferogram) is performed.

The recorded emission spectra show that the ratio of the atomic to molecular line intensities remains almost constant in time (at a fixed gas pressure) within the experimental uncertainty. Contrary to the observations in the RF discharge [11], in the investigated DC discharge the atomic to molecular line intensity ratio decreases with the pressure, being the highest at \( p = 200 \) mTorr (figure 2(a)). It may be speculated that the difference comes from the different discharge conditions, determining the possible channels for production of hydrogen atoms. In the RF discharge, H atoms originate mainly from dissociation of \( \text{H}_2 \). In the DC discharge, the nickel cathode acts as an additional source of H atoms when the desorption processes dominate over the adsorption. A significant contribution to the production of hydrogen atoms may be also expected from reactions between \( \text{H}_2 \) and ions accelerated in the electric field (see the discussion below). Favorable conditions for these channels are achieved at low pressures and high currents, i.e. high energy of the ions.

Significant differences in the processes leading to hydrogen atoms in both types of discharges are also detected through the interferometric measurements. Figure 2(b) presents a comparison between the fitted profiles of the \( \text{H}_2 \) line in the RF [11] and in the current DC source. As it could be expected, the narrow central peak, due to emission of thermal hydrogen atoms in both types of discharges, has comparable widths, corresponding to atomic temperatures of about 1000–2000 K (results from this study are shown in figure 2(g)). This emission follows the electron-impact excitation of thermalized ground state atoms arising from dissociation of \( \text{H}_2 \). The difference between the profiles emerges in the shape of the broad pedestal, although the widths are again comparable (about 10 eV). In the case of the RF discharge the pedestal is flat, which corresponds to emission from almost monoenergetic fast atoms [11]. The latter are products of various reactions passing through excited molecular states (see [11] and references therein). A specific feature of the DC discharges is the existence of a strong
electric field leading to acceleration of charged particles towards the cathode – this should be one of the important factors leading to the different appearance of the pedestal shape. The channels of great importance for production of fast excited hydrogen atoms in DC discharges are these with accelerated hydrogen ions taking part in a charge-exchange reaction with \( \text{H}_2 \) \[12,13\] and reflection of fast neutralized ions from the cathode \[9\]. Some of the ions on their way to the cathode collide with \( \text{H}_2 \) and produce fast excited hydrogen neutrals moving in the same direction. The rest of them reach the cathode, where they may neutralize or neutralize and fragmentize and, as a result of all interactions

![Diagram](image)

Figure 2. Comparison between emission spectra in the RF and DC discharges (a). Typical \( \text{H}_2 \) spectral line profile in the RF \[11\] and the current DC source (b). Change of the \( \text{H}_2 \) profile with the pressure (c). Time dependence of the ratio between thermal and fast atom densities (d). Time dependence of the relative densities \( n_{\text{th}} \) (e) and \( n_{\text{f}} \) (f). Time dependence of the temperature of thermal hydrogen atoms (g).
with the cathode, fast hydrogen atoms are directed back towards the anode. The ions may also sputter adsorbed hydrogen atoms with significant energies [9]. The fact that the pedestal width in this study stays almost constant (about 10 eV) suggests that the most important source of fast atoms is dissociation of molecular hydrogen (H₂ or H₂⁺) which leads to nearly monoenergetic fast atoms, while the change of the wings of the profile may be explained by the significant initial energy of the H₂⁺ ions accelerated in the DC electric field. These observations differ from those in the hollow cathode discharge in [13] operated at somewhat higher pressures (2.25–3.75 Torr), where the pedestal width is significantly broader (36–59 eV) and its FWHM changes with the experimental conditions.

Let us now look in more detail at the fitted Hα profiles from the DC discharge at the investigated gas pressures (figure 2(c)). The variation of the experimental conditions leads to changes in the ratio between the areas under the curves describing the central peak and the pedestal. This ratio reflects the ratio between the densities of the thermalized (nₜʰ) and the fast (nₓ) excited atoms. At higher pressures, the density of all types of particles is higher, leading to significant collision rates and a shorter mean free path. The energy of the accelerated ions is lower and the density of the fast atoms originating from reactions specific for the DC discharges is relatively low. Therefore, at high pressures the pedestal shape is flatter and is more similar to the shape at the RF discharge.

In order to clarify the importance of the interactions between the accelerated ions and the cathode one may follow the evolution of the Hα profile with the time. In figure 2(d), the ratio between the thermal and the fast excited atoms nₜʰ/n₅ is plotted as a function of the time. For the three working pressures the ratio drops, which means that the relative density of the fast atoms increases. This behavior cannot be explained by the charge-exchange reactions between ions and H₂ because the discharge conditions remain unchanged. The only parameters that change with the time are the temperature of the cathode and the amount of adsorbed hydrogen. As it was shown in [9], the reflection coefficient for hydrogen atoms from nickel depends on the amount of the adsorbed hydrogen on the surface, which is higher for a clean Ni surface. Due to the intensive desorption of hydrogen (see figure 1(b)) during the discharge, the density of the backscattered fast neutralized ions increases, which agrees with the experimental observations. The difference in the slopes of the three nₜʰ/n₅ dependences in figure 2(d) probably comes from the different desorption rates, which in turn should be associated with the faster increase of the cathode temperature at lower pressures.

From our experimental data it is also possible to assess the time dependence of the densities of the thermalized (nₜʰ) and the fast (n₅) excited atoms. They are proportional to the areas of the central peak and the pedestal (figures 2(e) and 2(f)). At 200 mTorr, both densities grow with the time, although (n₅) grows somewhat faster. At 500 mTorr, the density of the fast atoms grows, while the contribution of the thermalized atoms remains almost constant. At the higher pressure (p = 1600 mTorr), both densities are almost constant within the time interval observation. These observations again support the hypothesis that during the discharge operation the density of the fast atoms increases. Nevertheless, more work is needed in order to analyze the contribution of all possible reactions leading to production of fast atoms.

4. Conclusions
In this paper, experimental evidence is discussed supporting the hypothesis that in the coaxial DC source considered the NiH molecules are sputtered from the cathode surface. This hypothesis may help to explain the differences between existing sources and to optimize their working conditions. It turns out that it is important to keep the temperature of the cathode low to prevent the predominance of the desorption processes which reduce the density of NiH molecules on the surface.

The spectroscopic part of this study allows for additional characterization of the hydrogen neutrals in the present discharge source and for evaluation of the relative contribution of reactions leading to formation of excited H atoms. The analysis is in progress and the results will be reported in a separate study.
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Corrigendum: Investigation of the hydrogen neutrals in a discharge source used for production of metal hydrides

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Figure 2 a should be replaced by:

![Figure 2 a replacement](image-url)