UDK 533.9

PECULIARITIES OF APPLYING REVERSIBLE HYDROGEN GETTERS AS MATERIALS FOR CATHODES IN GAS DISCHARGE DEVICES

V. N. Borisko, I. A. Rudaya, I. N. Sereda
Kharkov National University. Physical technical department.
61108, 31 Kurchatov av., Kharkov,Ukraine

The peculiarities of applying cathodes made of reversible getter hydride-forming alloys in the gas-discharge devices with crossed ExH fields have been revealed. It has been shown that the availability of such electrodes allows to realize a correlation between the intensity of working gas releasing and the discharge parameters. The possibility for controlling erosion processes and heat regimes for the cathode materials has been shown to exist by initiating a controlled hydrogen desorption from the electrodes.

In systems of gas feeding for various plasma and energy physical devices using hydrogen isotopes as a working gas, the gas is generally injected into a discharge chamber from a tank through Pd or Ni accumulators which clean hydrogen from various gaseous impurities [1]. Recently, in the above systems, solid-state gas generators based on binary hydrides of such metals as Ti, Zr, Sc, Er, U, etc. have been widely used [2]. First of all, the advantages of those generators are a high purity of the gas injected (99,99 – 99,999%), along with the safety and compactness in storage. However, intermetallic compounds of the ST-707 and ST-172 type based on Zr-V, Zr-V-Fe, capable to absorb hydrogen reversibly, which were developed in Italy by "SAES Getters" Company [3, 4], allow to design universal gas supplying systems that combine the functions of not only a working-gas generator but a getter as well. At room temperatures, such intermetallic compounds exhibit the equilibrium pressure not exceeding 1 – 10 Pa, the dynamics of sorption-desorption and hydrogen capacity being improved. The decomposition of the hydride phases of the above materials allows to provide for filling hydrogen isotopes in the range of working temperatures 400 – 900 K, and t

he gas itself releases uniformly. The feature peculiar to those compounds is a decrease in the ionization potential of hydrogen generated by 0,3 – 0,5 eV caused by the recombination of hydrogen atoms at the metal-hydride surface following by the desorption of the molecules in the excited and thermodynamically non-equilibrium state [5, 6].

In recent years, the possibility for applying such materials as electrodes in gas discharge devices has been investigated [2, 7]. It has been found that the availability of the metal-hydride electrodes saturated with hydrogen decreases the combustion voltage in the self-maintained glow discharge which results from increasing in the hydrogen ionization cross-section by a

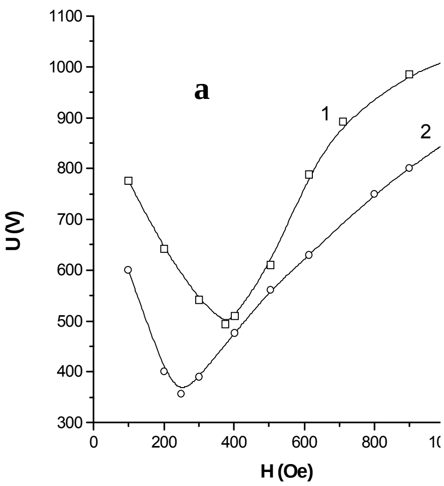

Fig.1a. The ignition curves of reflecting discharge.
1 – cathode from metal-hydride.
2 – cathode from stainless steel.

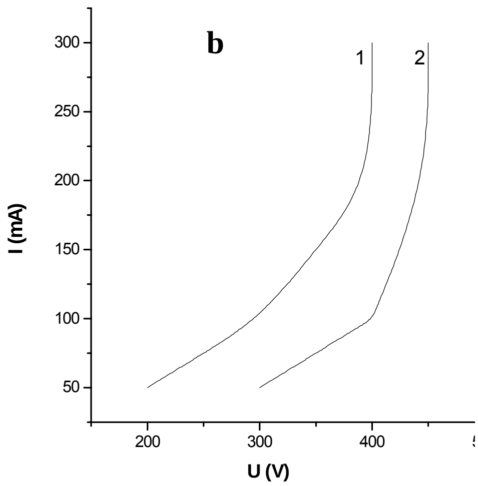

Fig.1b. Current–voltage characteristics of magnetron discharge.
1 – cathode from stainless steel.
2 – cathode from metal-hydride.

factor of 1,3 to 1,5 as compared to common molecular hydrogen from a tank. It has been also shown by mass-spectrography methods that in this case, the properties of the discharge gas phase change: the shares of H^+ and H^+_3 enhance relative to the content of the molecular ions H^+_2. However, the plasma parameters and the processes in plasma have not been studied. Besides, the investigations were only performed in the glow discharge, and some of the experimental results obtained were not simply interpreted and are of a contradictory character. Here, we summarize the experimental data presented on the influence of the metal-hydride cathode saturated with hydrogen on the follows. The cross-section for the process of dissociative adhesion of the low-energy electrons to the oscillatory excited molecules of the working gas is inversely proportional to the electron energy and increases also with increasing the oscillation quantum number of molecules [10]. Near the cathode, electrons have a minimal energy which fact is connected with turning the trajectories of the oscillating electrons in the reflecting discharge, as well as with the emission of the low-energy secondary electrons resulting from the ionic bombardment of the cathode. On the other hand, the metal-hydride cathode saturated with hydrogen desorbes the molecules which are already in the

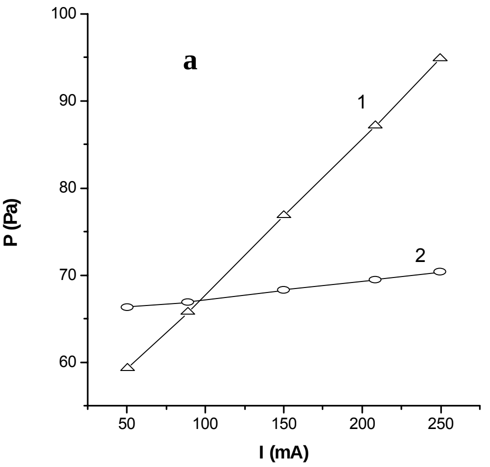

Fig.2a. Magnetron discharge. Dependence of hydrogen pressure in gas discharge devices.
1 – cathode from metal-hydride.
2 – cathode from stainless steel.

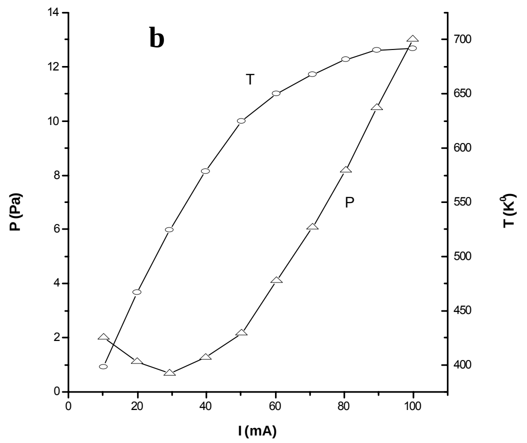

Fig.2b. Reflecting discharge. Dependence of hydrogen pressure (P) and metal-hydride cathode temperature (T) on the discharge current value.

gas-discharge characteristics, as well as the influence of the discharge plasma on the gas-emission properties of that electrode. The investigations were carried out in the discharges with crossed electrical and magnetic fields: the Penning and planar magnetron discharges. The discharge cathodes were made of the getter hydride-contained alloy $Zr_{55}V_{40}Fe_5$ modified with 3 mass percent B_2O_3 . For reference measurements, the cathodes from molybdenum or stainless steel were used. The two types of the discharge were investigated in the hydrogen medium, both in self-consistent in pressure regime [8, 9], in which case the increase in discharge current due to the power introduced into the discharge results in the increase in the hydrogen pressure inside the chamber, and the decrease in the above current lowers the pressure; and in the flow of hydrogen. Studies on the conditions for the existence of the discharge of both types in cases of applying the cathodes made of metal-hydrides or stainless steel, revealed that, unlike the findings of the previous authors, while the external parameters being the same, the ignition of the discharge with metal-hydride cathodes was worse than that with stainless steel ones, and the discharge voltage exceeded a similar value for the reference discharge (Fig. 1). The reasons are as oscillatory excited state. Therefore, these processes near the cathode lead to the significant increase in the cross-section for generating the negative ions and, as a consequence, to the deterioration of the ignition and increase in the discharge-supporting voltage. To verify the above assumption, a possibility for creating a source of the negative hydrogen ions which could use the reflective discharge with a metal-hydride cathode for a plasma-forming stage has been investigated [11]. The comparative analysis performed on the negative hydrogen ions yield in case of using the cathodes made of a hydride-forming material and stainless steel showed that the usage of the above intermetallic compounds allowed to enhance significantly the current in the H-beam. The mass-spectrometry of the neutral plasma component in the magnetron discharge burning in hydrogen atmosphere which is desorbed from the metal-hydride cathode showed that the insertion of such a compound into the cathode of a gas-discharge device changed markedly the composition of not only the main plasma gas component but also the impurity one, i. e. in this case, various plasma-chemical reactions involving hydrogen are stimulated [9]. The changes in the composition of the gas-phase impurities are not connected with the emission of the hydrogen atoms from the metal-hydride cathode surface, i. e. such a cathode also features the catalytic activity in reactions accompanied with the hydrogen transmission.

Fig. 2 displays the dependence's of the working-gas pressure on the discharge current for discharges operating in the autostable in pressure regimes. For comparison, in Fig. 2a, curve 2, the change in the hydrogen pressure in the discharge chamber with a stainless steel cathode is plotted. From Fig. 2 it can be seen that in a magnetron discharge, the presence of a metal-hydride cathode leads to the significant change in pressure in the discharge chamber, and the dependence itself is linear. For the reflecting discharge, when one of the cathodes was made of the metal-hydride saturated with hydrogen and the other was made of stainless steel, the above dependence is non-linear at low discharge currents (up to 50mA) and near - linear at $I_d >$ 50mA. The reason is that the mechanism of the interaction between cathodes and discharge gas phase is changed. Within the low discharge current range, the dispersion of the cathode material made of stainless steel by high-energy particles and the absorption of hydrogen by the resultant film are crucial. However, as the discharge current and, consequently, the temperature of the cathodes enhance, the role of the hydrogen desorption from the metal-hydride cathode is growing (Fig. 2b) The plasma parameters for the discharges of both types were determined by the probe technique. In the planar magnetron discharge, the measurements were performed at the height of 0,5cm under the anode section in the points positioned under the area of plasma beam location.

The electron temperatures in the discharges with the cathodes of both types appeared to be the same: $T_e \sim 2$eV. However, the dependence's of the plasma density on the discharge current significantly differed (Fig. 3).

In case of discharge with the metal-hydride cathode, the plasma density was monotonously growing as the discharge current increased, whereas for the reference discharge, the tendency for saturation was observed.

The presence of the metal-hydride cathode causes the gas density within the near-cathode region to be determined by the dynamical equilibrium between sorption and desorption processes which depends on the temperature and hydrogen-sorbing characteristics of the hydride-forming material. Therefore, in this regime, increasing the hydrogen pressure, as the discharge current is rised, is accompanied by increasing the gas density in the discharge chamber. The resultant gain in the rate of collisions between electrons and neutral particles leads both to the intensive ionization processes and to the enhancement of the diffusive electron flow from the area of the plasma beam localization. For this reason, the increase in the discharge current with the metal-hydride cathode is accompanied by the rise in the plasma density beyond the electromagnetic trap. The investigation on the spatial distribution of the plasma parameters within interelectrode clearances in the Penning discharge for cathodes made of stainless steel and hydrogen-saturated metal-hydride showed that both the space potentials and the electron temperature did not depend on the cathode material. However, within the near-cathode areas, the plasma densities are observed to differ by a factor of 2 - 3. In the area of the metal-hydride cathode, the plasma density is slightly lower which fact seems to be connected with the processes of recharging positive ions at the molecules of hydrogen desorbed from that cathode.

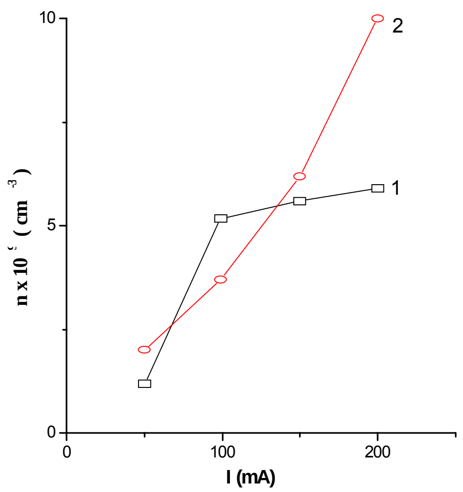

Fig.3. Dependence of plasma density on the discharge current value.
1 – control discharge.
2 – discharge with metal-hydride cathode.

The explorations on the dispersing of the metal-hydride cathodes in the regime of hydrogen desorption were carried out. The cathodes were irradiated with argon and hydrogen ions with energies (0,5 - 5) keV and current densities (10 - 100) mA/cm^2 . The analysis revealed the significant decrease in the erosion as compared to the dispersion of the same materials with no desorption. As can be seen from Fig. 2, the hydrogen desorption from the metal-hydride cathodes has a unique functional dependence on the discharge current. In other words, the bombardment of the discharge of the metal-hydride cathode with high-energy plasma particles is an effective tool for controlling the gas-emission regime of its operating. As a result, close to the cathode surface, the protective gas target is formed which reduces markedly the erosion of the material due to the dissipation on it of the particle-beam energy.

In the Penning discharge, the temperature of the cathodes was controlled by thermocouples, one of the electrodes being made of the metal-hydride saturated with hydrogen and the other being made of stainless steel. The increase in the discharge current was observed to slow down the growth in the temperature of the metal-hydride cathode (Fig. 2b, curve T). The analysis of the thermal balance showed that the major portion (up to 70%) of the heat energy released at the cathode was expended on the desorption of gaseous hydrogen. Such a softening of the thermal regime during the operation of the electrodes made using reversible hydrogen sorbents with high rates and large thermal effects of sorption-desorption was achieved due to both the heat decomposition of the hydride phases and energy dissipation of the particle beams on the gas target which was formed with the hydrogen desorbed.

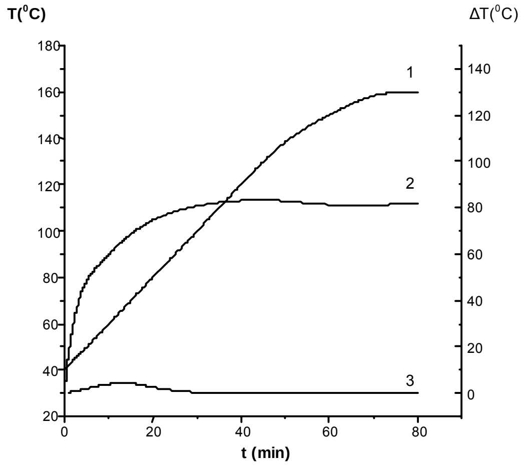

Fig.4. Dependence of metal-hydride temperature (1) and difference of temperatures between cathodes (2 – metal-hydride – stainless steel, 3 – metal-hydride – metal-hydride) on the exposition time.

The dependence of the difference between the operating temperatures for the cathodes on the exposition time for the bombarding the hydrogen particles with the energy 2,5 kV and current density 5 mA/cm^2 plotted in Fig. 4 shows that the temperature of the metal-hydride cathode is significantly lower than that of the stainless steel one, and in case of using two metal-hydride cathodes, a minor temperature difference is observed only during the first 15 minutes of the discharge operation, then it completely disappears.

As a result of the studies performed, it has been shown that applying the reversible sorbents of hydrogen at a low pressure with high rates and large thermal effects of sorption-desorption allows to reduce significantly the rates of their dispersion by the plasma ions as well as to lower the heat load for those materials. The above effect is achieved due to creating the protective gas target as a result of both thermal decomposition of the metal-hydride and ionic stimulated desorption. The influence of the plasma beams upon those cathodes stimulates the hydrogen desorption from the electrode immediately into the operation zone of the plasma-forming stage which fact provides a return coupling between the intensity of the gas emission and parameters of the gas discharge.

The application of the reversible hydrogen getters as cathodes for the plasma sources of the negative ions permits to enhance significantly the negative ion yield owing to the desorption of the molecules in the oscillatory excited state from those materials.

References

1 G. V. Grekova., A.V. Kobelev, G.G. Lokshin Vodorodnij natekatel dlya moshnih gazorazryadnih priborov // Pribori i tehnika experimenta. 1984, vol. 1, P. 219 – 220.

2. A.V. Bastiev, M.A. Obolenskij, V.V. Solovej. Aktivaciya vodoroda i vodorodosoderjaschih energonositelej. Kiev: “Naukova dumka”, 1993, 162 p.

3. P. Della Porta, C. Pizani. Non-evaporable gettering pumps. // SAES Getters, Techical Reports, vol. 8-16, Milano (Italy), 1969.

4. A. Barosi, T. A. Giorgi. A non-evaporable getter for low temperatures. // Vacuum, 1973, vol. 23, № 1, P. 15 – 19.

5. S.B. Valuiskaya, M.V. Lotockij, L.P. Scripal i dr. Issledovanie processa “aktivacii” vodoroda metallogidridami. II Massspectrometricheskoe opredelenie potenciala i secheniya ionizacii vodoroda // VANT. Ser. Yadernie tehnika i tehnologiya. 1989, vol. 1, p. 58–61.

6. Yu.F. Shmal’ko, Ye.V. Klochko, N.V. Lototsky. Influence of isotopic effect on the shift of the ionization potential of hydrogen desorbed from metal hydride surface // Int. J. Hydrogen energy, 1996, vol. 21, p. 1057–1059.

7. S.A. Galchinskaya, V.V. Dorohov, N.D. Lazarev i dr. Issledovanie processa “aktivizirovaniya” vodoroda metallogidridami. I. Mass-spectrometricheskij analiz plasmi tleyushego razryada // VANT. Ser. Yadernaya tehnika i tehnologiya, 1989, vol. 1, p. 55–58.

8. Ye.V. Klochko, M.V. Lototsky, V.V. Popov, Yu.F. Shmal’ko, V.N. Borysko. Investigation of plasma interaction with metal hydride. // Int. J. Hydrogen Energy. 1999, vol. 24, p. 169–174.

9. Ye.V. Klochko, M.V. Lototsky, V.V. Popov, Yu. F. Shmal’ko, V.N. Borysko. Sorption and electrotransfer characteristics of hydrogen – gettering materials in contact with a hydrogen plasma. // J. Alloys and Compounds. 1997, vol. 261, p. 259–262.

10. M. Capiteli. Neravnovesnaya kolebatelnaya kinetika. M: “Mir”, 1989, 392 p.

11. V.N. Borisko. Plazmennij istochnik otricatelnih ionov vodoroda // Visnik HGU, Ser. Yadra, chastinki, polya. №421, p. 146–148.