Application of Metal Hydrides For Gas Handling In Hydrogen Masers*

Harry T. M. Wang
Hughes Research Laboratories
Malibu, CA 90265

Summary

Reversible interaction of hydrogen with certain metals and alloys have beem employed to effectively satisfy the hydrogen supply and flow regulation, as well as vacuum maintenance requirements of a hydrogen maser. In addition to providing significant reductions in maser size, weight and power consumption, the hydride components also lead to improved system reliability. A hydrogen supply for seven years of operation of an oscillating compact maser can be stored in 50 grams of $LaNi_5$ or $LaNi_{4.7}Al_{0.3}$. The source occupies a volume of less than 50 cc, including an electrically controlled palladium-silver alloy flow regulator. A combination getter-ion vacuum pump system for the maser was developed using a zirconium graphite getter. Operational experience indicates that for reliable maser operation, a clean, bakeable vacuum system design is a critical requirement.

Introduction

The operation of the hydrogen maser requires a steady supply of state selected hydrogen atoms. Furthermore, signal-to-noise ratio and atomic transition linewidth considerations dictate that the atomic resonance be observed in a high vacuum environment. In conventional maser designs atomic hydrogen is obtained by dissociating hydrogen molecules in a radio frequency discharge. The supply of molecular hydrogen is typically stored in a vessel under high pressures. A sputtering ion pump is used to pump away the spent gas and other outgassing products to maintain the required high vacuum for maser operation. Both the pressure vessel (and the associated flow regulator) and the ion pump having the capacity to handle the gas load alone are bulky components which constitute a significant portion of the size and weight of the maser. For field operable devices, and especially devices for spaceborne applications, size, weight and power consumption are important considerations. Moreover, the ion pump has been trouble prone, causing reliability problems. Indeed, most maser failures are traceable to ion pump malfunctions. It is therefore desirable to eliminate the ion pump, or at least minimize its role in maser vacuum maintenance.

Many metals and alloys react reversibly with hydrogen to form compounds termed hydrides. The great affinity for hydrogen and other properties of selected metals and alloys can be exploited to provide effective remedies for gas handling and vacuum maintenance requirements in the atomic hydrogen maser. In this paper, we will discuss a hydrogen supply and a vacuum pump for the maser employing hydride interaction.

Hydrogen Storage Using Hydrides

The technique of hydrogen storage in hydrides makes use of the reversible reaction of a solid metal, M, with gaseous hydrogen, H_2, to form a solid metal hydride, MH_x, according to the equation,

$$\frac{2}{x} M + H_2 \rightleftharpoons \frac{2}{x} MH_x + heat \quad .$$
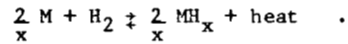
The reversible reaction means that hydrogen can be stored or discharged at will, analogous to a water sponge or a rechargeable electric battery. At a given temperature, T, the equilibrium dissociation pressure, P, for a charged hydride is relatively constant, at least in theory.[1] In practical storage media, the dissociation pressure may depend on the hydrogen content, as shown by the hydrogen absorption and desorption characteristics of a 50 gram sample of $LaNi_{4.7}Al_{0.3}$ at room temperature in Figures 1 and 2. On the other hand, the dissociation pressure is a sensitive function of temperature and is described by the van't Hoff equation,

$$\frac{d(\ln P)}{d(1/T)} = \frac{\Delta H}{R} \quad ,$$

where ΔH is the heat of reaction and R is the gas constant. For a specific application, the storage medium is selected to satisfy working temperature and pressure requirements.

Recent metallurgical advances had made a variety of media suitable for hydrogen storage readily available. Some hydrides and their hydrogen storage characteristics are shown in Table I. Hydrogen density in a gas at a pressure of 100 atmospheres and in liquid hydrogen are also shown for comparison. It is
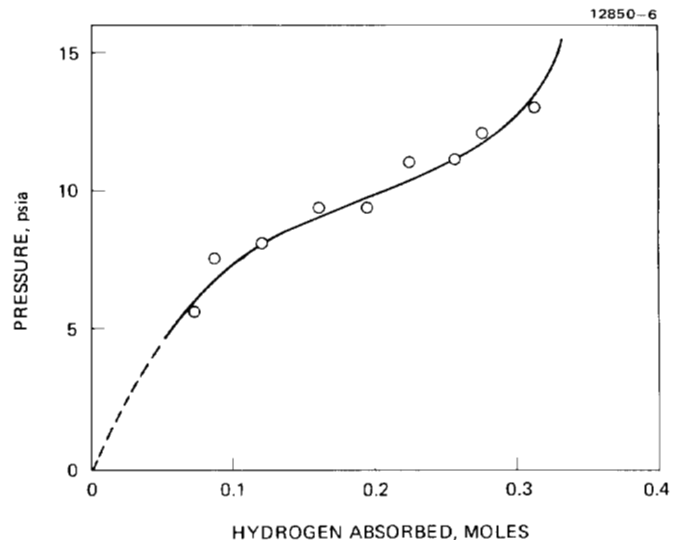

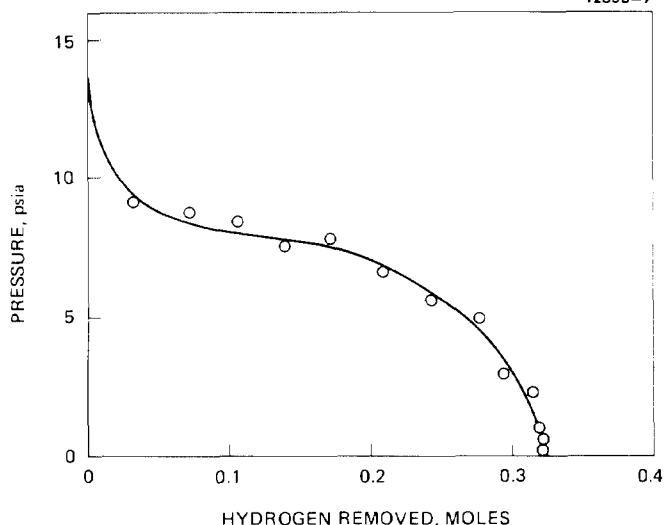Figure 1. Hydrogen storage in $LaNi_{4.7}Al_{0.3}$: Absorption (50 grams sample).

Figure 2. Hydrogen storage in LaNi$_4$.$_7$Al$_0$.$_3$: Desorption (50 grams sample).

TABLE 1. Hydrogen Storage in Metal Hydrides

MEDIUM	HYDROGEN CONTENT		DISSOCIATION PRESSURE AT 25 °C, atm	HEAT OF REACTION H, kcal/mole-H
	wt% H	H-atom/mL x 10^{-22}		
U - UH$_3$	1.3	8.3	2.5 x 10^{-9}	-20.2
Mg - MgH$_2$	7.6	6.7	5.5 x 10^{-7}	-18.5
LaNi$_5$ - LaNi$_5$H$_6$	1.5	7.6	1.65	-7.4
LaNi$_{4.7}$Al$_{0.3}$ - LaNi$_{4.7}$Al$_{0.3}$H$_6$	1.4	7.2	0.42	-8.1
H$_2$, GAS AT 100 atm	100	0.5	–	–
H$_2$, LIQUID	100	4.2	–	–

interesting to note that volume for volume, the solid hydrides have hydrogen contents greater than that in liquid hydrogen. Needless to say, the hydride storage is more energy efficient and incomparably safer than liquid hydrogen. Uranium hydride has been used to provide spectroscopically pure hydrogen samples. However, since both uranium and uranium hydride are pyrophoric in finely divided form, they present handling problems. Besides, to obtain hydrogen at reasonable pressures, the hydride has to be heated to high temperatures. The requirement of elevated temperatures also applies to magnesium and other similar binary hydrides which otherwise provide a very favorable hydrogen density to weight ratio.

Several hydrides have been used to provide a hydrogen supply for the maser.[2] We have chosen to investigate mischmetal hydrides as possible maser hydrogen storage media. The technique has a number of desirable features:

(1) high density hydrogen storage, leading to a compact and lightweight package; (2) automatic purification of hydrogen during the charging and discharging cycle; and (3) dissociation occurring at room temperature at a pressure of the order of one atmosphere. Thus, neither a bulky mechanical regulator (for high gas pressure) nor a power consuming heater (for hydrides with too low a dissociation pressure) is needed; and (4) the discharge is endothermic, making hydride storage inherently safer than pressure vessel storage. In addition, due to the low hydrogen flow rate in the maser, no external heater is required.

Our experimental investigations centered on LaNi$_5$ (HY-STOR 205) and LaNi$_4$.$_7$Al$_0$.$_3$ (HY-STOR 207).[3] The capacity of these hydrides is such that the hydrogen supply for 7 years operation of an oscillating compact hydrogen maser can be stored in about 50 grams of the materials, occupying a volume of about 7 cc. Hydrogen storage characteristics for a 50 gram sample of LaNi$_4$.$_7$Al$_0$.$_3$ are shown in Figures 1 and 2. The data were taken at room temperature. A prototype hydrogen supply for the maser using LaNi$_5$ was successfully tested on an operating maser. Even though the dissociation pressure of LaNi$_5$H$_6$ is only 1.6 atmosphere at 25°C, the exponential dependence on temperature according to the van't Hoff equation means that it will increase to 20 atmosphere at 100°C. To simplify container design, a hydride with lower dissociation pressure would be more desirable. HY-STOR 207 (LaNi$_4$.$_7$Al$_0$.$_3$) was found to satisfy the requirements. The hydride can be charged at relatively low pressures (about 1 to 2 atmospheres at room temperatures). The dissociation pressure of the hydride at 25°C is only about 0.4 atmospheres, increasing to about 7 atmospheres at 100°C. A hydrogen supply system for the maser including an integrated palladium-silver alloy flow regulator is shown in Figure 3.

The Pd-Ag flow regulator is another example of the application of hydriding interaction to maser gas handling requirements. Hydrogen permeates the wall of the Pd-Ag tube. The flux, J, per unit area, A, is proportional to the concentration gradient, dc/dr of hydrogen in the alloy.

$$J/A = -D dc/dr \quad .$$

The diffusion coefficient, D, obeys Arrhenius relation,

$$D = D_0 \exp(-E_a/kT) \quad .$$

For Pd-Ag (80/20) alloy, $D_0 = 3.4 \times 10^{-3}$ cm^{2}s^{-1} (Ref. 1), and the activation energy $E_a = 5.35$ kcal gm-atom^{-1}. The exponential dependence on temperature of the hydrogen permeation rate is conveniently used to provide an electrically controlled hydrogen flow for the maser.

Getter Pump for the Maser

Chemical getters have been widely used in high vacuum systems and electronic tubes. Until recently, they have not been seriously considered for use in the maser. This is probably due to the fact that the more familiar evaporable getters are inconvenient to use and have very limited capacity.

During the last several years, we have investigated the suitability of non-evaporable getters for maser applications. The aim of our experimental investigations is to gather data on getter pump characteristics and to determine maser vacuum system design criteria.

The non-evaporable zirconium graphite (ST-171)[4] getter we shall discuss here has very attractive features: (1) tremendous capacity and pumping speed for hydrogen; and (2) hydrogen gettering (hydriding), after activation, occurs at room temperature without any power consumption. These features will lead to a compact and lightweight vacuum pump. On the other hand, the pumping speed of the getter for other outgassing products in the system at room temperature is very limited. The requirement of the maser is best met by a combination vacuum pump system consisting of a getter and a small ion pump. The
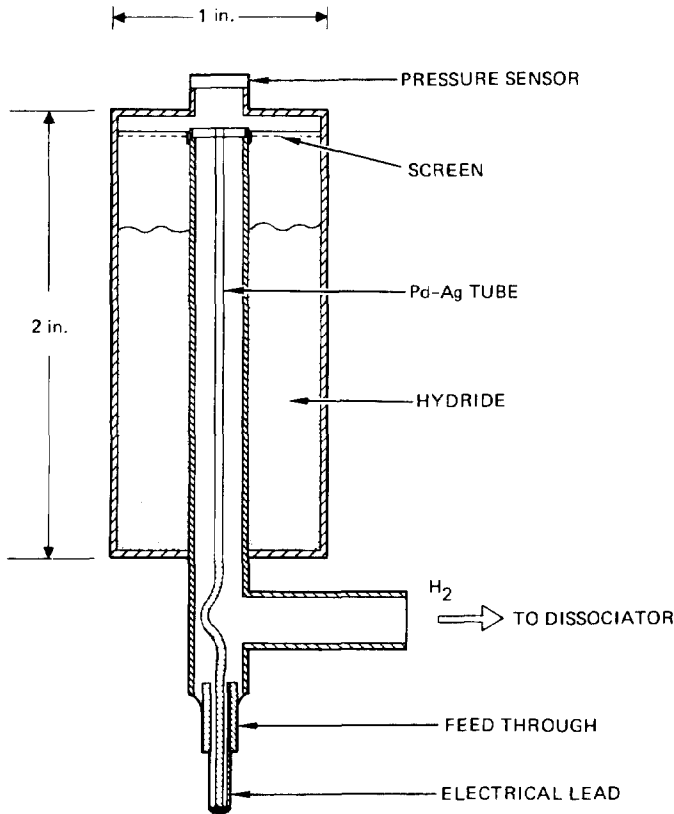
Figure 3. Schematic of a maser hydrogen
supply with an electrically
controlled Pd-Ag flow
regulator.

Figure 4. Schematic of a getter pump test
station.

getter handles the dominant hydrogen gas load while
the ion pump evacuates the non-getterable
contaminants.

A schematic of the getter pump developmental
test station is shown in Figure 4. Our zirconium
graphite getter test sample is in the form of a
hollow cylinder, 40 mm O.D. x 25 mm I.D. x 46 mm long
and weighing 100 grams. It is housed in a quartz
container attached to an all-metal vacuum
system using a flanged moly-quartz transition. The
transparent container allows visual observation of the
physical condition of the getter. The test station is
provided with an ionization gauge for pressure monitor-
ing, a quadrupole mass spectrometer for residual gas
analysis and a 2 liter/sec appendage ion pump for an
evaluation of the ion pump behavior under large hydro-
gen flow conditions. Molecular hydrogen is admitted to
the test chamber through a voltage controlled Pd-Ag
alloy flow regulator. Hydrogen flow rate is determined
from pressure changes in a reservoir of known volume.
A capacitance manometer with a digital readout is used
for precise reservoir pressure reading. A liquid
nitrogen roughing pump is used for initial pump down
through a bakable metal sealed valve. Prior to getter
activation and data collection, the system is baked out
under high vacuum. A combination ion and titanium
sublimation pump is used during high vacuum bake out
and subsequent getter activation.

An effective activation procedure was established
as follows. Using an external oven, the getter is
heated to about 925°C under high vacuum. The tempera-
ture is raised gradually so that getter outgassing does
not overload the ion-titanium sublimation pump system.
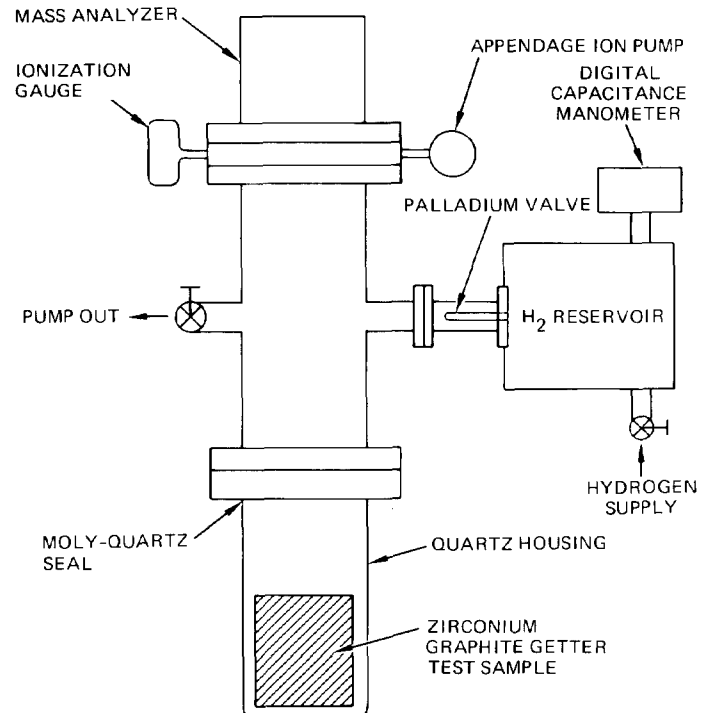After reaching 925°C, the temperature is held constant

until residual pressure in the test chamber is about
10^{-6} Torr or less. This usually requires one working
day to complete. By comparison, the manufacturer's
recommended procedure could be completed in a fraction
of an hour after attaining the 900°C activation tem-
perature. Our experience is that the latter procedure
does not provide optimum pumping speed and capacity but
is probably adequate if repeated activation is desired.

In order to obtain the desired capacity data
within a reasonable interval, hydrogen throughput is
accelerated to about 30 times the normal flow rate in
an oscillating compact maser of about 2.3×10^{-5} Torr-
liter/sec. Data for a 100 gram zirconium graphite
getter sample is shown in Figure 5. Some interesting
observations are:

(1) The getter has tremendous capacity for hydro-
gen. The 100 gram sample can pump more than 10^4 Torr-
liters of hydrogen. This is to be compared with an
estimated hydrogen consumption of about 5×10^3 Torr-
liters in seven years of normal oscillating compact
maser operation.

(2) The initial pumping speed is very high. Even
though it falls off with the amount of hydrogen pumped,
the pump can be designed to easily meet maser
requirements.

(3) The deviation from exponential decrease in
pumping speed after pumping about 1500 Torr-liters of
hydrogen is probably due to enlarged surface area of
the getter due to cracking and flaking. Powder forma-
tion was observed after the getter absorbed a few
hundred Torr-liters of hydrogen. A photograph of the
getter after absorbing about 5000 Torr-liters of hydro-
gen is shown in Figure 6. Powder confinement is a
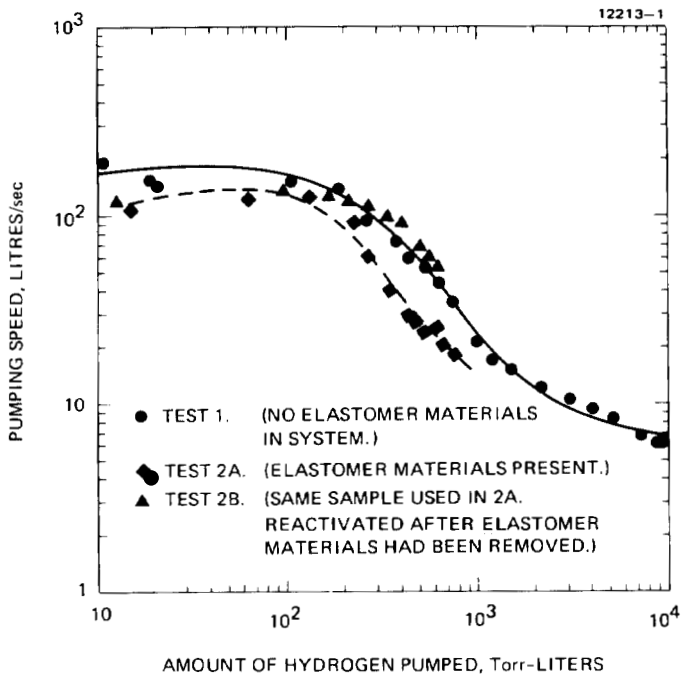critical requirement for maser getter pump design.

9

Figure 5. Zirconium-graphite getter pump characteristics, with or without the presence of elastomers in the system.

Figure 6. Photograph of a 100 gram zirconium-graphite getter sample after pumping about 5000 Torr-liters of hydrogen.

(4) Elastomers have a deleterious effect on getter pump operation, as can be seen from a comparison of data for Tests 2A and 2B shown in Figure 5. Test 2A used a fresh getter sample. A viton O-ring and a small sheet of teflon were purposely inserted in the vacuum chamber. These elastomers were chosen because they are used in conventional maser designs. Data were taken only after bake out at about 100°C for one day followed by a few days observation, with no hydrogen gas load, to ascertain that the system has completed the initial high rate of outgassing. The lower pumping speed of the getter in the presence of elastomers is obvious from the data shown in Figure 5. To confirm this result, the elastomers were removed from the test chamber. The same getter sample was reactivated by the normal procedure and its pumping characteristics measured. The results obtained denoted as Test 2B are in excellent agreement with those obtained in Test 1.

(5) Despite the large hydrogen throughput, the 2 liter/sec ion pump operated normally in the clean test station. That is, there were no significant pump current instabilities, as can be seen in Figure 7 which shows the ion pump current and ion gauge readings during the course of a test. Since both readings are proportional to the system pressure, differing by a calibration factor, the tracking of the two sets of readings, and therefore the stability of the ion pump current, is indicated by their difference shown in the bottom curve of Figure 7. (The ion pump was not operating during Test 2A and 2B to avoid masking the deleterious effect of the elastomers we were trying to observe. As we will see below, the elastomers are probably detrimental to ion pump operation as well.)
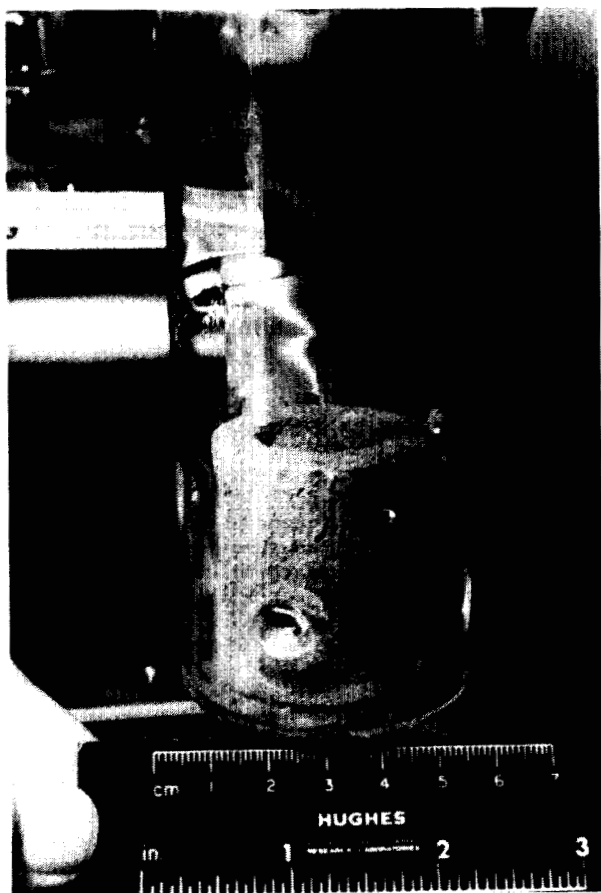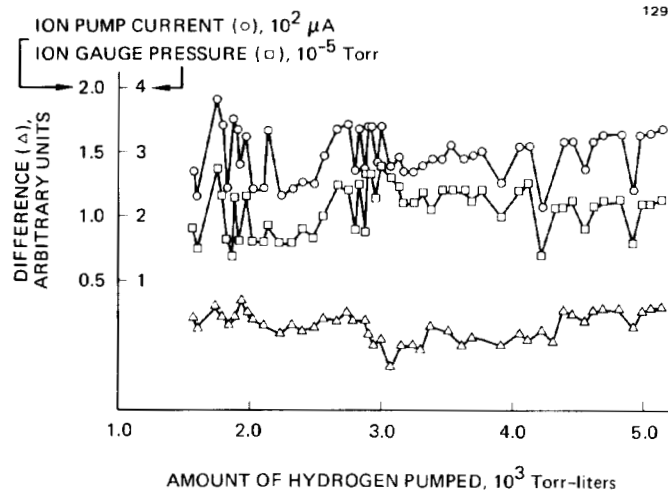

Figure 7. Ion pump current and ion gauge readings during a getter capacity test. The good tracking of the two sets of readings reflects stable ion pump operation in a clean system in the presence of large hydrogen throughput.

Combination Getter-Ion Pump System Operational Experience

Combination zirconium graphite getter and ion pump systems were used on our prototype oscillating compact masers, CHYMNS-I and II,[5] with varying degree of success. The getter pumps were activated in situ after high vacuum had been established in the maser using an external pump. Immediately after getter activation, the background pressure was at its lowest point and rose gradually in time, as indicated by an increase in

the ion pump current. We first attempted to explain this behavior as being due to degradation in the pumping speed of the getter pump. Since CHYMNS-I and II employed viton O-rings and had not been baked to high temperatures, the degradation could presumably be accelerated. However, this does not explain the observed instability in the ion pump, which occurred in 3- to 6-month intervals, and the technique we employed to rejuvenate the system. For example, when ion pump instability occurs, the system can be brought back to normal stable operation without the use of an external pump. The procedure consists of operating the ion pump power supply in the start mode and letting a controlled amount of hydrogen into the maser to cause a thermal run-away in the ion pump. The hydrogen supply is then shut off while the ion pump undergoes a self bake out. The high temperature will force most of the hydrogen absorbed in the electrodes of the ion pump to be released. Thus, the system pressure would rise. In a few hours, the background pressure would begin to fall, and in due course, the ion pump would begin to function, leading to a stable operating high vacuum again. This would be good for another 3- to 6-month cycle. Note that without another pump to evacuate the gas released from the hot ion pump, the ion pump could not start to function. Thus, the getter pump must still be functioning to absorb the hydrogen and reduce the background pressure to enable the ion pump to function again. This technique had been successfully repeated.

As noted earlier, we have not observed any ion pump instabilities in our clean getter pump development test station, although the hydrogen throughput is at least an order of magnitude higher than in the maser. The main difference is the absence of elastomers in the getter test station and the fact that it has been baked out at high temperatures under high vacuum conditions. This suggests that elastomers may be deleterious not only to getter pump operation but also to ion pumps as well. This is due to the fact that hydrogen pumping in ion pumps is predominantly by diffusion into the cathode rather than by chemical combination at the anode, such as occurred for heavier molecular species. (The light hydrogen ions produce comparatively little sputtering.) Therefore, surface conditions and permeability of the cathode are critical factors in hydrogen pumping. The former is, of course, a sensitive function of gas composition in the system. This discussion points out the importance of eliminating, or at least minimizing the presence of, elastomers from the maser vacuum system. Cleanliness and high temperature bakeout capability are critical requirements of the maser vacuum system design.

Conclusion

Reversible interaction of hydrogen with metals and alloys can be exploited to effectively solve the gas handling problems in hydrogen masers. A prototype of a maser hydrogen source employing hydride storage techniques has been successfully tested. With regard to application of getter pumps in the maser, several design problems such as powder confinement and getter poisoning remain to be solved. If size and weight are not critical considerations, zirconium aluminum alloy (ST-101)[4] may be a more suitable getter. The large surface area resulting from spraying the powdered getter on a large mechanical support makes the getter more resistant to poisoning. Knowing the design criteria, the problems are not insurmountable. We believe that getter pumps will contribute to greatly improved reliability, along with smaller size, lower weight and power consumption in the maser.

Acknowledgments

References

1. G. Alefeld and J. Volkl, Editors, Hydrogen in Metals II (Springer-Verlag, New York, 1978).

2. R.F.E. Vessol et al., Proc. 8th Annual PTTI (1976); H.E. Peters, Proc. 34th Annual Freq. Control Symp. (1980), p. 360.

3. "HY-STOR" is a trade name of Ergenics, Wyckoff, N.J.

4. "ST-171" and "ST-101" are trade names of SAES Getters, Colorado Springs, CO.

5. H.T.M. Wang, "Characteristics of Oscillating Compact Masers," Proc. 36th Ann. Symp. on Freq. Control (1982), pp. 249-254.