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1

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AUTHOR(S): T. Ide, K. Okuno, S. Konishi, F. Sakai, H. Fukui, M. Enoeda and Y. Naruse
Japan Atomic Energy Research Institute

J. L. Anderson and J. R. Bartlit
Tritium Science & Technology Group
Materials Science & Technology Division

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$LaNi_3Mn_2$ ALLOY AS A TRITIUM STORAGE MATERIAL

T.Ide, K.Okuno, S.Konishi, F.Sakai, H.Fukui, M.Enoeda and Y.Naruse
Japan Atomic Energy Research Institute
Tokai-mura, Ibaraki-ken, 319-11 Japan

J.L.Anderson and J.R.Bartlit
Material Science & Technology Division
Tritium Science & Technology Group
Los Alamos National Laboratory
Los Alamos, NM 87545

Summary

An all metal apparatus has been constructed and installed in the main cell of the Tritium System Assembly (TSTA) at Los Alamos National Laboratory, as a separate experiment, to handle about 2600 Ci of tritium for study of metal tritides of potential application for storing tritium in fusion fuel processing. The apparatus is similar to that used for protium/deuterium gas[1] but some modifications were made to assure safe handling of tritium.

The pressure-composition isotherms for the $LaNi_3Mn_2$-protium (H), deuterium (D) and tritium (T) system were measured to study isotopic effects in the temperature range of 60 ℃ to 250 ℃, the pressure range below 120 kPa.

Introduction

There is an increasing interest in materials able to store and supply tritium gas safely. Metal hydride technology is suited for the handling and processing of tritium gas. Uranium is famous and common as a tritium storage material. Uranium however has certain disadvantages in handling because of its high chemical reacivity and legal restrictions due to nuclear material. The knowledge of the pressure-composition isotherm data is of importance for its possible application in fusion fuel prossesing and for the safe storage of large tritium amounts as metal tritides.

An all metal apparatus has been constructed and installed in the main cell of the Tritium System Assembly (TSTA) at Los Alamos National Laboratory, as a separate experiment, to handle about 2600 Ci of tritium for study of metal tritides. At first the $LaNi_3Mn_2$-T system was chosen to measure the pressure composition isotherms. $LaNi_{5-x}Mn_x$-H systems were examined in the previous experiments[1] as shown in Fig. 1. $LaNi_3Mn_2$ alloy was known to have following features.

- Large capacity of hydrogen isotopes.
- Low equilibrium pressure at room temperature
- High pressure at moderate temperature
- Constant pressure during release of hydrogen
- Practical ab/desorption kinetics
- Stability in air at room temperature
- Easy handling and activation
- Variety of equilibrium pressures by change of Mn substitutions

$LaNi_3Mn_2$ alloy can be employed for the interim storage and transport of tritium gas. Activated $LaNi_3Mn_2$ alloy reacts with hydrogen at room temperature within minutes below atmospheric pressure. Equilibrium pressure at room temperature is estimated to be 4 Pa at the composition of $LaNi_3Mn_2H_2$.

In this paper the first measurements of $LaNi_3Mn_2$-T system of the pressure composition isotherms are reported to confirm availability for tritium service. The results are compared with the data for protium and deuterium using the same sample under the same experimental conditions.

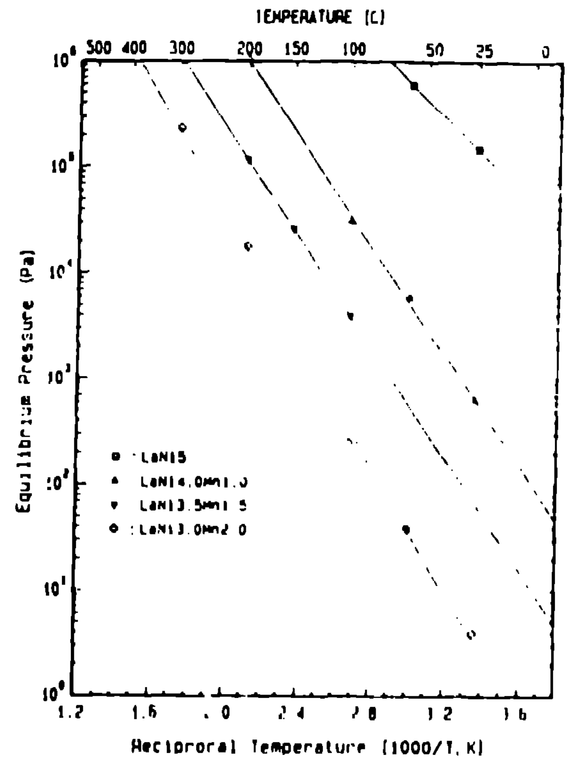


Fig.1 Plot of plateau pressures against reciprocal temperature for $LaNi_{5-x}Mn_x$ hydrides

Experimental Apparatus

Pressure composition isotherms were measured with the apparatus shown in Fig. 2. The apparatus is similar to that used for previous experiments,[1] but some modifications were made to assure safe handling of tritium. The apparatus consists of an automatic equilibrium pressure measurement section, a tritium storage/supply bed filled with $LaNi_3Mn_2$ alloy, a circulation pump and a dry vacuum system with a quadrupole mass spectrometer. The entire apparatus is placed in a glovebox except the vacuum system.

The major components of the equilibrium pressure measurement section are a sample cell, tanks, capacitance manometers and an automatic data acquisition/control system with a computer [illegible]. The components have been designed for tritium gas service. The tritium storage/supply bed and sample cell are surrounded by a [illegible] stainless steel container in order to capture the permeated tritium. Tanks with thermocouples are used for measuring the amount of tritium absorbed/desorbed in the sample. A metal bellows double containment pump is used to circulate the gas in the loop when [illegible] blanketing has [illegible] [illegible] the experiment is exhausted to the tritium waste treatment system [illegible] column packed with $LaNi_3Mn_2$ alloy.

Tritium source using $LaNi_3Mn_2$ alloy, 2600 Ci source of our design, is shown in Fig. 3. All welded structure was adopted in primary vessel. The equilibrium pressure over the $LaNi_3Mn_2$-T system in the two phase region is several Pa at room temperature. The tritium can be released from the $LaNi_3Mn_2$ powder to the desired pressure by heating the heater in 30 minutes. The T equilibrium pressure at 270℃ is about 100 kPa. Helium-3 owing to tritium decay was removed from the source gas periodically. A sample cell for measurements of $LaNi_3Mn_2$-H, D and T systems is shown in Fig. 4. The structure of the sample cell is almost the same as the tritium source except number of nozzles.

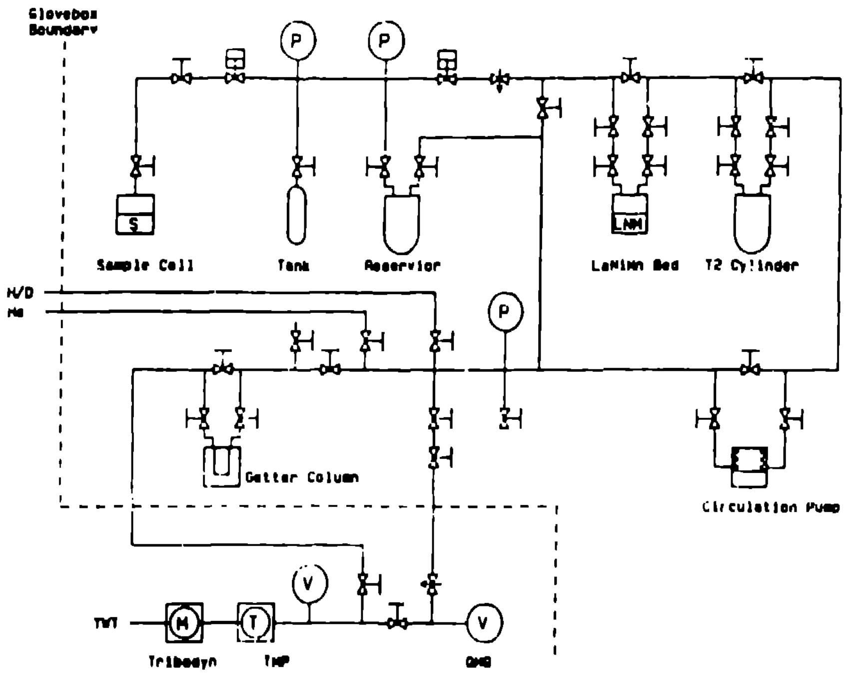
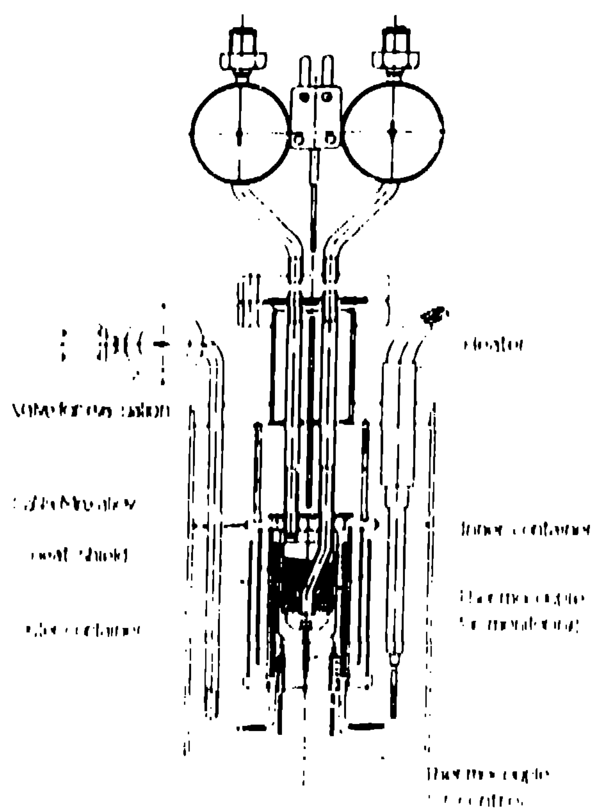
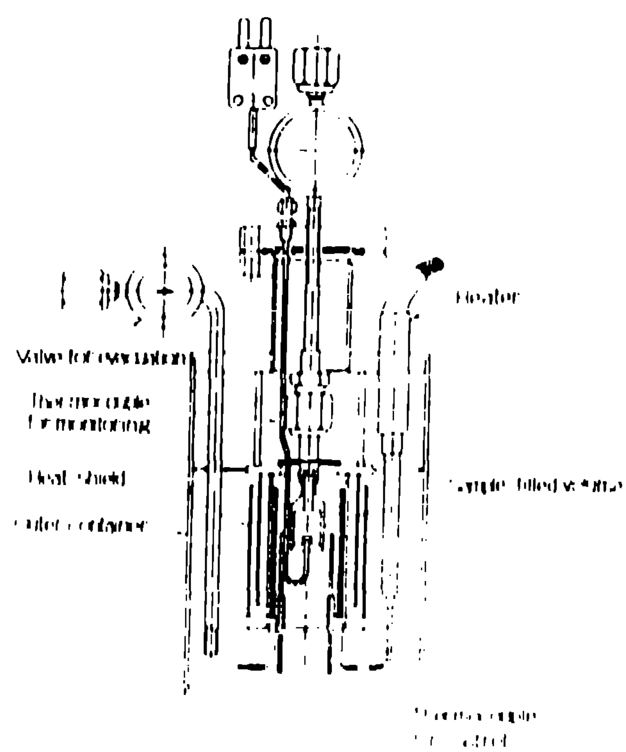


Fig.2 A schematic diagram of metal tritide study.





Materials

The $LaNi_3Mn_2$ alloy was prepared by induction melting of the elemental metals in an argon atmosphere. All the elemental metals used were commercially pure, with purities 99.7% for La, 99.9% for Ni and 99.9% for Mn. After two meltings the alloy was annealed at 750 ℃ under argon atmosphere for ten hours. The bulk composition of the alloy corresponds to the formula $La_{1.01}Ni_{3.01}Mn_{1.98}$. The main impurity is 100-ppm carbon as detected by X-ray fluorescence analysis. The alloy ingot was crushed into granules under argon atmosphere. 2-gram was prepared for the measurements of the pressure-composition isotherms.

For the isotopic study, the purity of the H gas was 99.999 vol.%. The D gas was about 99.7% pure with most of the residual 0.3% being H_2 and HD. The purity of the T gas used was 97.5 at.% and 2.5 at.% D. Purity of the T gas was analysed by a mass spectrometer in the TSTA.

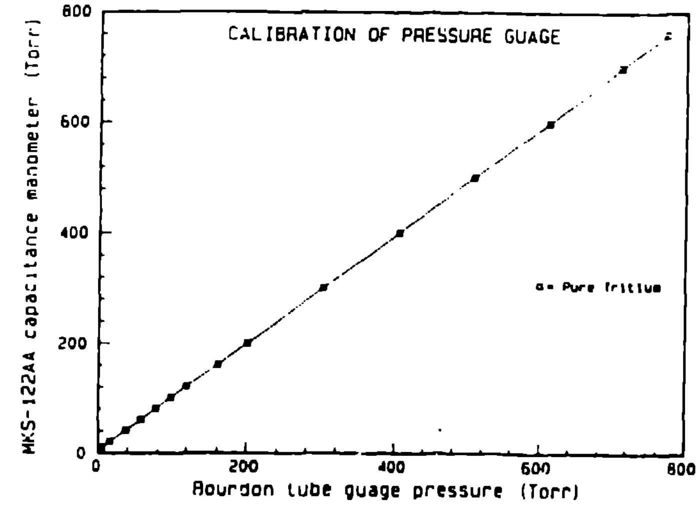


Fig.5 Calibration result of capacitance manometer.

Experimental Procedure

For the determination of the equilibrium pressure of the T gas, capacitance manometers with 1000 and 10 Torr full scale sensors were employed. To check the correct pressure measurement of capacitance manometer, calibration was carried out using a Bourdon-tube guage (Wallace & Tiernan, model FA145, 0-1500 Torr). Fig. 5 shows a comparison of pressures of the Bourdon-tube guage and MKS 122AA capacitance manometer. Readings of both pressure guages agree within ±0.5% differences in the pressure range of 10-760 Torr. No effects of tritium on pressure measurements using MKS capacitance manometer were confirmed.

A 16-mesh $LaNi_3Mn_2$ alloy sample was activated by exposure to atmospheric hydrogen at room temperature followed by evacuation over 3 hours at 300 ℃. Absorption reaction started rapidly at room temperature. When absorption was completed, the sample was dehydrided under vacuum at 300 ℃. After several absorption-desorption cycles, the pressure-composition isotherms at desired temperature were measured.

The H, D and T compositions in the sample were calculated from conventional PVT measurements. This measurements and calculation was made automatically by the HP integral computer. The experiments using H, D and T were performed separately with the same sample and the same conditions. The sample and pressure measurement section were degassed for two days to eliminate isotopic exchange effect before each new isotope experiment.

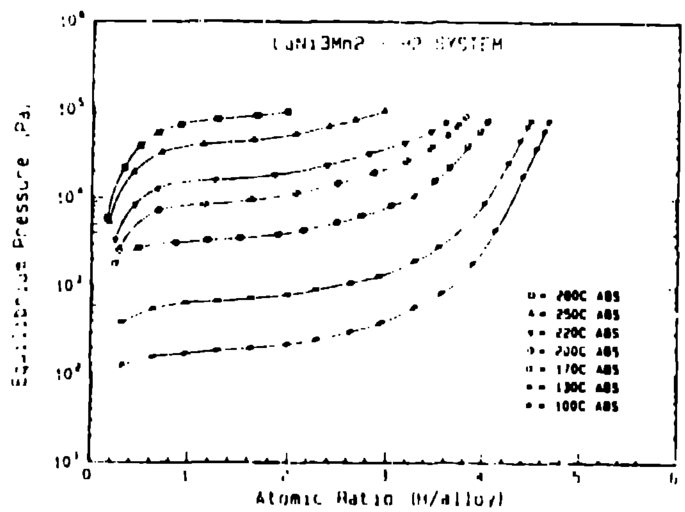


Fig.6 Absorption isotherms of $LaNi_3Mn_2$-H system

Pressure Composition Isotherms

Absorption pressure composition isotherms for the $LaNi_3Mn_2H$, $LaNi_3Mn_2D$, $LaNi_3Mn_2T$, in the concentration (y) range (0.20 ≤ y ≤ 5.0), pressure (p) range ([illegible] ≤ p ≤ 120 kPa) and temperature (T) range ([illegible] ≤ T ≤ 250 ℃) are shown in Fig. 6-8. The equilibrium pressures of H and D are slightly lower than those obtained in the previous experiments. This will be due to a little difference of alloy composition of the samples because manganese substitution in $LaNi_5$ brings great effects of lowering equilibrium pressures as shown in Fig. [illegible] There is a slight slope in the plateau shown in Fig. 6-8. [illegible] and [illegible] have shown that homogenization anneal make the plateau of [illegible] Mn, alloy more level and well developed.

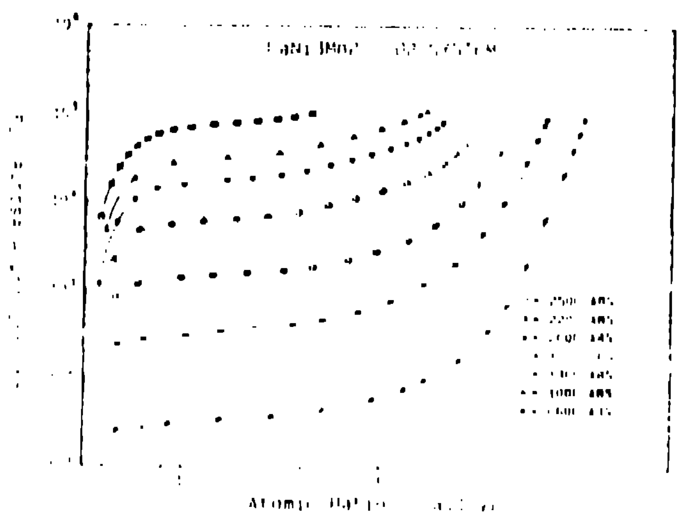


Fig.7 Absorption isotherms of $LaNi_3Mn_2$-D system

Fig. 9 shows a comparison of the plateau pressures for H, D and T at 170 and 220 ℃. The comparison of the pressures of the hydrogen isotopes shows $p_T > p_D > p_H$ at the same temperatue and the same concentration. As an example, the $p_H/p_D/p_T$ ratio at 220℃ is about 1/1.8/2.4 in the plateau region. These plateau pressures, obtained at about the middle of each sloping plateau (y= 2), are plotted for all the isotherms as a function of reciprocal temperature in Fig. 10. The logarithmic pressure and the reciprocal temperature have a linear relationship represented by eqn. (1), (2) and (3) for H, D and T respectively.

$$\ln p_H \text{ (Pa)} = 24.19 - 7027/T \text{ (K)} \quad (1)$$

$$\ln p_D \text{ (Pa)} = 24.79 - 7025/T \text{ (K)} \quad (2)$$

$$\ln p_T \text{ (Pa)} = 24.98 - 6989/T \text{ (K)} \quad (3)$$

Desorption isotherms, generally used for calculating thermodynamic properties of metal-hydrogen system, were also measured and will be reported elsewhere. There was a little hysteresis effect between absorption and desorption isotherms similar to that observed in the previous $LaNi_{5-x}Mn_x$-H systems[1].

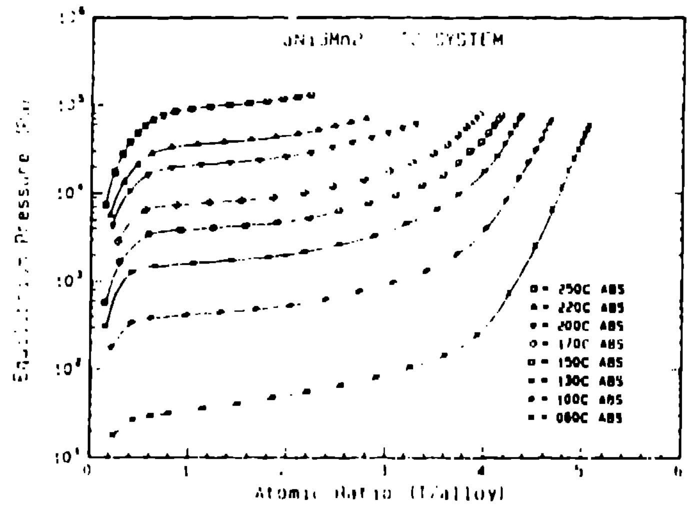


Fig. 8 Absorption isotherms of $LaNi_3Mn_2$ T system.

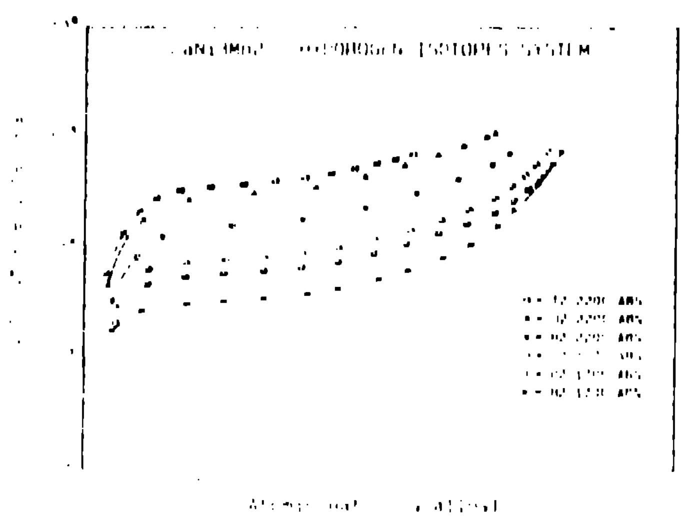


Fig. 9 Absorption isotherms of $LaNi_3Mn_2$ for H, D and T

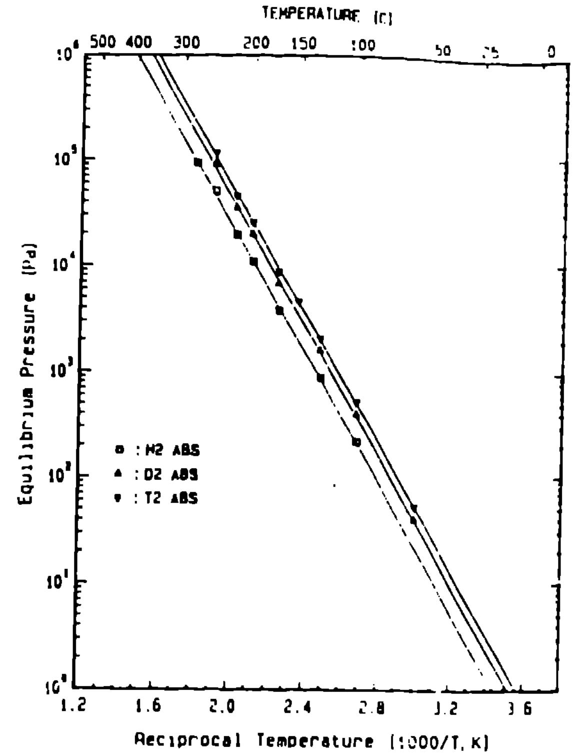


Fig.10 Absorption plateau pressures $LaNi_3Mn_2$ for H, D and T.

Conclusions

The pressure-composition isotherms for the $LaNi_3Mn_2$-protium, deuterium and tritium with the same sample and the same experimental conditions were obtained. In the measured temperature, concentration and pressure ranges the equilibrium pressures of each hydrogen isotope show $p_T > p_D > p_H$ at the same temperature and concentration. $LaNi_3Mn_2$ alloy would be a useful material for tritium storage.

Further informations on practical use such as cyclic performance, aging effect on alloy structure due to helium retention would be necessary for long term storage.

References

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[2] C. E. Lundin and F. E. Lynch, "Modification of Hydriding Properties of AB_5 Type Hexagonal Alloys through Manganese Substitution", Miami Int. Conf. Alternative Energy Sources 8, 3801 (1978)