MCM·325L(CP)

LONG-TERM BEHAVIOR OF THE TRITIDES FORMED BY NICKEL-BASED INTERMETALLIC COMPOUNDS

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ABSTRACT

Some properties of the tritide phases formed by the intermetallic compounds Mg_2Ni, $ZrNi$, and $LaNi_5$ have been studied. Whereas $ZrNiT_3$ will retain its stoichiometry indefinitely when sufficient gaseous tritium is available, the stoichiometries of Mg_2NiT_4 and $LaNi_5T_{6.9}$ decrease with time. Although all three intermetallic tritides can retain large quantities of the helium-3 tritium decay daughter product in the solid phase, irreversible release of helium begins after several hundred days for $ZrNiT_x$ and Mg_2NiT_x. However, $LaNi_5T_x$ retains all of the helium generated in the solid for at least 2400 days. NMR measurements for $ZrNiT_x$ and Mg_2NiT_x imply that helium is retained in microscopic bubbles as previously observed in several binary metal tritides.

INTRODUCTION

During the past decade or so, many intermetallic compounds and their alloys have been found to reversibly absorb and desorb gaseous hydrogen. These alloys are being considered for various applications such as chemical storage beds, getters, isotope separation, pressure pumps, and purification systems in the support of hydrogen combustion and nuclear fusion technologies. The most promising intermetallic alloys for these applications have the general compositions A_2B, AB, AB_2, and AB_5 where metal A (e.g., Ti, Zr, Mg, La, etc.) forms very stable hydride phases and metal B (e.g., Ni, Fe, Mn, etc.) is usually an endothermic absorber of hydrogen. Although the effects of tritium decay and helium (^3He) formation have been studied in several binary tritides,[1-9] apparently little information is available for similar properties in any intermetallic tritide. The present paper describes the long-term behavior (i.e., data have been obtained for periods that exceed six years) on the ternary tritides Mg_2NiT_4, $ZrNiT_3$, and $LaNi_5T_{6.5}$, which can be regarded as representative examples of tritides formed by intermetallic types A_2Ni, ANi, and ANi_5. Most attention has been on the abilities of these tritides to maintain their stoichiometries as the tritium atoms radioactively decay and the retention of the inert gas ^3He daughter product in the solid phase. These studies have indicated considerable variations for these tritides which are most likely related to differences in structural, chemical, and mechanical properties. Some general trends have been identified and are compared to past observations[1-9] on various binary tritides.

EXPERIMENTAL DETAILS

The ternary metal tritides had been prepared by direct reactions of tritium (about

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98-99% T_2) gas with intermetallic compounds from commercial vendors. Because the $ZrNiT_x$ and Mg_2NiT_x materials have low dissociation pressures at room temperature, master batches of these tritides were synthesized for distribution into several storage containers for periodic gas sampling by volumetric-mass spectrometric methods and the nuclear magnetic resonance (NMR) experiments. However, the high-dissociation pressures and expected rapid desorption rates[10] for $LaNi_5$ hydrides required in-situ preparation of individual $LaNi_5T_x$ samples on a common high-pressure gas manifold. Most of the Mg_2NiT_x and $ZrNiT_x$ samples had an initial tritium gas overpressure of about 3 bars. However, one gas sampling container of each material, as well as all the NMR samples, were initially sealed under vacuum. Both $LaNi_5T_x$ samples had an initial tritium pressure of 9 bars immediately after synthesis. The stoichiometry retention and helium release from the solid phases were monitored by periodic analysis of the gases removed from a small (i.e., less than 5% of the total free volume) sampling station on each container. All of the samples were kept at room temperature. Standard transient NMR techniques[3-4] were used to determine the triton and ^{3}He relaxation times T_1 (spin-lattice), T_2^* (lineshape decay), and T_{2m} (spin-spin). Each NMR sample was ultimately analyzed via a thermal desorption method[3-6] where the final temperature was nominally 1000°C and the compositions of evolved gases were determined by mass spectrometry.

RESULTS AND DISCUSSION

The initial stoichiometries of the intermetallic tritides were determined to be $ZrNiT_{2.93}$, $Mg_2NiT_{3.95}$, and $LaNi_5T_{6.3}$ which are in good agreement with the reported maximum compositions for the corresponding hydrides. The effects of time on the tritide stoichiometries and helium release behavior are summarized in Figs. 1 and 2, respectively. The three intermetallic tritides are seen to exhibit distinctly different behavior. Although no change was detected in

the Mg_2NiT_x stoichiometry upon the addition of gaseous tritium, stoichiometry increases for both $ZrNiT_x$ and $LaNi_5T_x$ were observed at the first sampling. While the increase was less than 2% for the $ZrNiT_x$ samples, it was nearly 10% for the $LaNi_5T_x$ sample shown in Fig. 1 and over 4% for the other $LaNi_5T_x$ sample. Because both $LaNi_5T_x$ samples had already experienced a prior tritium absorption-desorption cycle, they were assumed to be reasonably well-activated. Hence, the further increase in $LaNi_5T_x$ stoichiometry reflects either the formation of more tritide phase from a portion of the alloy that had not been originally activated or slow additional absorption to higher concentrations during the 16 days before the first samplings. Because most previous preparations[11-13] of the $LaNi_5H_x$ phases are usually considered to be complete within a few hours, the more gradual absorption as seen for $LaNi_5T_x$ probably was not recognized in the earlier work.

When the tritides were kept without excess tritium gas, their stoichiometries decrease quite closely to the predicted loss from tritium decay. The scatter in the thermal desorption data shown in Fig. 1 for approximately 900-day old Mg_2NiT_x is believed to reflect experimental difficulties rather than inhomogeneous variations in stoichiometry. In the presence of sufficient tritium gas, $ZrNiT_x$ was found to maintain its stoichiometry throughout the course of the present study while the stoichiometries of the other intermetallic tritides decreased. However, an apparent reversal of the stoichiometry decrease in Mg_2NiT_x was observed after about 1000 days, although this tritide had returned to only 90% of its original stoichiometry after 1800 days. From Fig. 2, it is clear that significant helium release also started for the Mg_2NiT_x samples after 800 days.

The following scenario is proposed for the Mg_2NiT_x behavior: A surface barrier (e.g., a layer of various oxides) exists on the
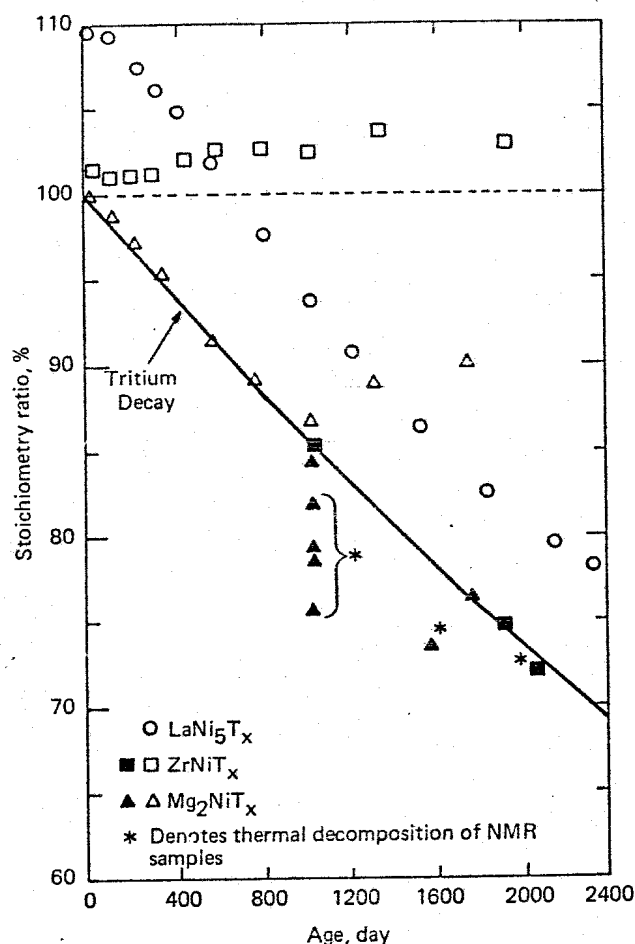
Fig. 1 - Effects of time on stoichiometries of metal tritides with excess tritium gas (open symbols) and initially stored under vacuum (closed symbols). Results have been normalized to initial composition at date of synthesis. Full line denotes stoichiometry change caused by tritium decay alone.

Fig. 2 - Cumulative helium (^{3}He) released from the metal tritides. The open symbols correspond to samples maintained with excess tritium gas while closed symbols represent samples initially under vacuum. The asterisk (*) denotes results from thermal desorption analyses on NMR samples.

as-prepared Mg_2NiT_x and prevents the absorption of gaseous tritium to either potentially increase its initial stoichiometry or replenish tritium in the tritide lattice that had radioactively decayed. Consequently, the Mg_2NiT_x stoichiometry steadily decreases until the onset of substantial helium release from the solid which presumably occurs through the
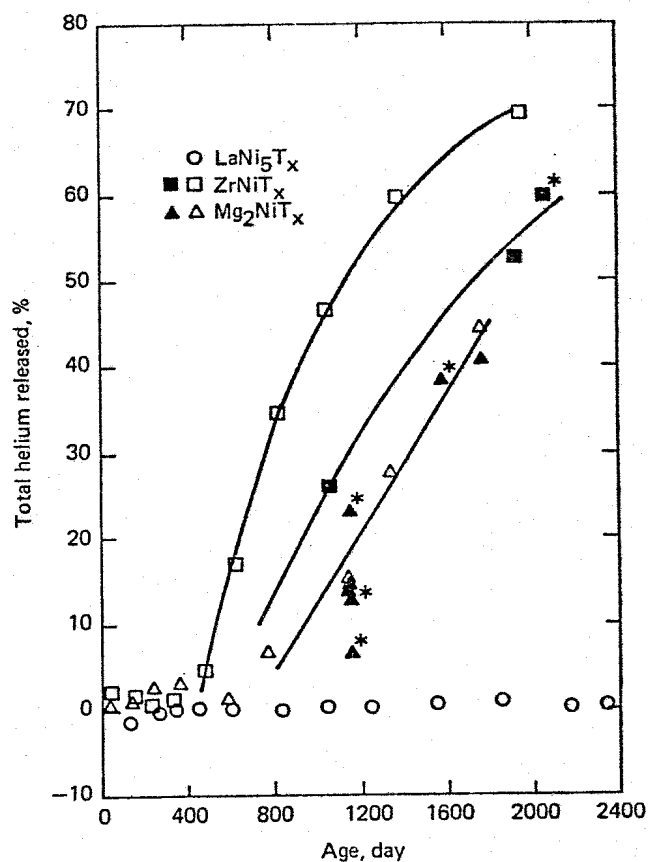
irreversible rupture of helium bubbles.[3] The helium release processes caused fractures in the impermeable oxides films which subsequently exposes either reactive surfaces or channels for the absorption of tritium to give the stoichiometry increase. Because the Mg_2NiT_x stoichiometry had not returned its initial composition by at least 1800 days, helium release has either

not occurred uniformly throughout the particles or regions remained blocked to the tritium gas. More information on the surface and defect properties of the Mg_2Ni hydride phases is required to clarify this behavior. Apparently, the $ZrNiT_x$ surfaces are sufficiently active to permit tritium absorption prior to any significant helium release.

Because the absorption-desorption reactions of $LaNi_5H(D)_x$ are quite rapid,[14] the stoichiometry decrease for $LaNi_5T_x$ cannot be attributed to surface barriers even though no helium release has occurred before at least 2400 days. The high equilibrium pressures for $LaNi_5$ hydrides[11-13] imply continual stoichiometry decreases as the tritium partial pressure falls. The room temperature isotherms for $LaNi_5H_x$ are shown in Fig. 3 along with pressure-composition data for the two $LaNi_5T_x$ samples. The $LaNi_5H_x$ desorption curve of Huston from INCO was generated from the master batch of alloy that was used to prepare these tritide samples. Several significant differences are immediately apparent. First, the tritium pressure over the high $LaNi_5T_x$ compositions is far below the projected hydride isotherms. This is not likely to be strictly an isotope effect since Biris et al.[11] found little difference between the hydride and deuteride isotherms. Unfortunately, there does not appear to be any available published isotherms for $LaNi_5T_x$ that were obtained by conventional methods.[11-13] Second, the partial tritium plateau pressures over the $LaNi_5T_x$ samples also exceeded both the absorption and desorption isotherms of the well-activated $LaNi_5H_x$ systems. When most of the tritium overgas was removed from one $LaNi_5T_x$ sample (i.e., No. 129) by a rapid expansion into an external volume to produce a reduced T_2 pressure of 0.6 atm, a sampling performed the next day showed that the pressure had only returned to 1.5 atm, which was about a fourth of the value prior to removal of the overgas. This tritium gas had been evolved from the tritide phase.
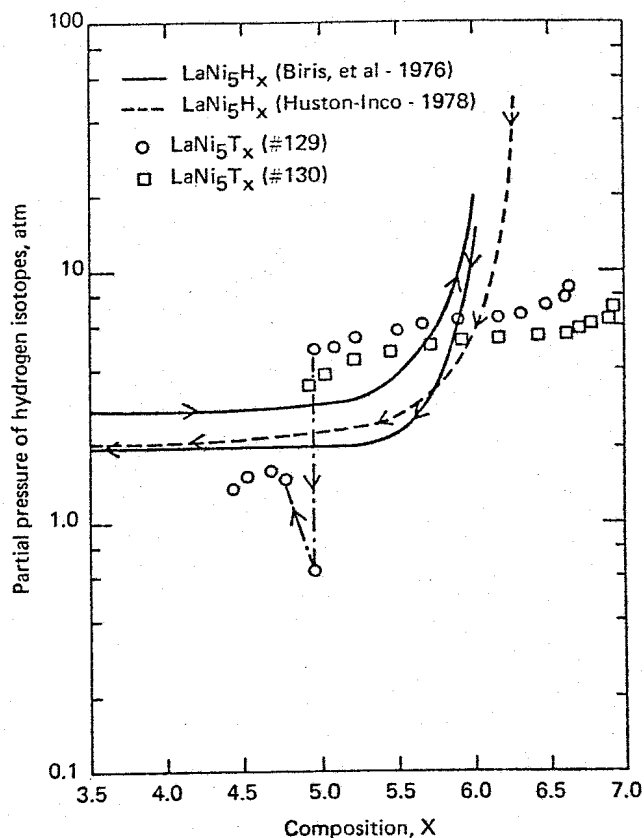

Fig. 3 — Portion of the room temperature (298K) pressure-composition isotherms for $LaNi_5H_x$ from the studies of Biris, et al.[11] and the unpublished data of the vendor (INCO) who had provided the alloy used to prepare $LaNi_5T_x$. Symbols for $LaNi_5T_x$ samples represent results obtained over a 6.5 year period. See text for details.

Subsequent measurements over the next fifteen months indicated that the partial tritium pressure for sample No. 129 remained below the published hydride desorption isotherm. However, the tritium partial pressure of the other $LaNi_5T_x$ sample (i.e., No. 130) had decreased only slightly over this period and still exceeded the hydride absorption isotherm as shown in Fig. 3.

Flanagan and co-workers[12-13] have recently described very interesting effects of annealing and hydrogen aliquot size on the plateau pressures and hysteresis behavior in the $LaNi_5H_x$ system. They found that annealing activated $LaNi_5$ alloy or decreasing the hydrogen aliquot size significantly increased the absorption-desorption hysteresis ratio by raising the absorption isotherm and depressing the desorption isotherm. Although this behavior is not completely understood, it has been associated[12,13] with the ability of the metal lattice to dissipate the mechanical stresses involved during the absorption or desorption of hydrogen. The removal of dislocations and other lattice defects by anneals as well as the reduced heat exchanges in small aliquot size lead to much larger hysteresis[12,13]. Since the normal absorption-desorption reactions for the $LaNi_5T_x$ samples are governed by 12.3 yr half-life of tritium, their isotherms will correspond to an extremely small aliquot size. Hence, from the previous $LaNi_5H_x$ observations[12,13] it is believed that the $LaNi_5T_x$ data in Fig. 3 represent the upper bound of the absorption isotherm and the lower limit for desorption after the tritium pressure had been dropped below the equilibrium isotherm. Contributions from the defects generated by the helium retention in $LaNi_5T_x$ may also be important but cannot be assessed from the available data. Systematic tritium isotherm measurements on well-characterized $LaNi_5$ alloys are needed to determine whether helium effects are significant.

The manner in which metal tritides retain helium as well as the means of subsequent helium release have been of interest for a long time[1-9]. From NMR studies[3-6] of ^3He relaxation times in several binary tritides it was proposed that most helium is contained in small gas bubbles (i.e., diameters of about 10 nm or smaller) and that release occurs through rupture of the largest bubbles when their pressures exceed the mechanical strengths of the damaged tritide lattice. Recent high resolution transmission electron microscopy experiments[7-9] have verified that 1-2 nm bubbles do exist in 100-400 day old tritides. Some T and ^3He relaxation time data for Mg_2NiT_x, $ZrNiT_x$, and several representative binary metal tritides are summarized in Table 1. The T relaxation times for all the materials except $VT_{0.50}$ correspond to immobile spins as expected for the known diffusion behavior of the hydride phases. The relatively rapid tritium mobility in $VT_{0.5}$ has been previously described.[6,15] All the ^3He relaxation time data in Table 1 are seen to obey

$$T_2^* < T_{2m} < T_1 \tag{1}$$

that was attributed[3,4] to helium retention in small bubbles where collisions with the bubble walls dominate the ^3He relaxation times. The increase in the T_{2m} and T_1 relaxation times, as well as the T_{2m}/T_1 ratio with sample age, is evident in Table 1 and corresponds to bubble growth as the trapped helium content becomes larger. Fig. 4 shows systematic increases in the ^3He T_{2m} and T_1 relaxation times for Mg_2NiT_x that are very similar to the age dependences previously found[3,5,6] for ^3He relaxation times in UT_x, TiT_x, and VT_x. Consequently, it is concluded that helium retention occurs in growing bubbles for most (if not all) metal tritides. A comparison of the time for significant helium release from Mg_2NiT_x as shown in Fig. 2 with the essentially constant ^3He relaxation times measured after 1000 days provides further support for the release of helium through the rupture of gas bubbles when they approach a critical dimension as was previously proposed in other systems.[3,6]

The triton T_1 relaxation times in Mg_2NiT_x were found to decrease as the sample became older. Similar behavior has not been noted in the other tritides listed in Table 1. A possible explanation is the production of paramagnetic relaxation centers in Mg_2NiT_x

Table 1. Representative ^{3}He and triton (T) relaxation times T_2^* (lineshape spin-spin), T_{2m} (CPMG spin-spin), and T_1 (spin-lattice) for several metal tritides. The resonance frequency for both spins is 45.7 MHz and all data were obtained at room temperature.

Initial Composition	Age (Days)	Spin	T_2^* (ms)	T_{2m} (ms)	T_1 (ms)	T_{2m}/T_1
$Mg_2NiT_{3.95}$	334	T	0.022	–	1,200	–
$Mg_2NiT_{3.95}$	1285	T	0.014	–	483	–
$Mg_2NiT_{3.95}$	403	^{3}He	0.175	13.8	2,800	0.005
$Mg_2NiT_{3.95}$	1281	^{3}He	0.330	615	14,600	0.042
$ZrNiT_{2.93}$	1517	T	0.019	–	260	–
$ZrNiT_{2.93}$	1330	^{3}He	0.153	127	8,920	0.014
$TiT_{1.88}$	1274	T	0.011	–	231	–
$TiT_{1.88}$	168	^{3}He	0.049	0.9	500	0.002
$TiT_{1.88}$	1346	^{3}He	0.093	135	2,240	0.060
UT_3	150	^{3}He	0.020	1.1	35	0.031
UT_3	1108	^{3}He	0.024	32.3	93	0.35
$VT_{0.50}$	1534	T	0.065	0.127	23	0.006
$VT_{0.50}$	140	^{3}He	0.061	2.9	530	0.005
$VT_{0.50}$	1825	^{3}He	0.076	54	2,240	0.024

because of tritium radiolysis. There was, however, no indication from the tritium lineshapes or spin-spin relaxation times for the formation of trapped molecular tritium in Mg_2NiT_x as previously found in the radiolytic decomposition[5] of LiT. It is possible that free magnetic Ni species are generated in Mg_2NiT_x, because Mg_2NiH_4 is known[16,17] to be a semiconductor rather than a traditional metallic hydride.

ACKNOWLEDGEMENTS

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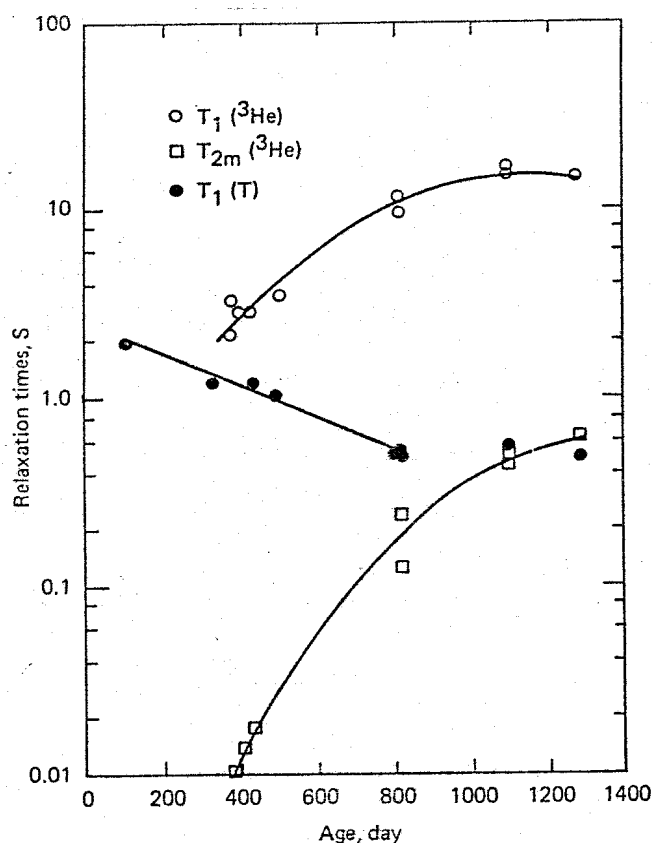Fig. 4 – Age dependent behavior of triton T_1 and ^{3}He T_1 and T_{2m} relaxation times for Mg_2NiT_x samples. These parameters were measured at room temperature where the resonance frequency was 45.7 MHz.

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