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Aging characteristics of Zr–V–Fe getters as observed by Mössbauer spectroscopy

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Abstract

Changes in the chemical environment of iron in Zr–V–Fe getters, as a function of hydriding–dehydriding cycles and exposure to impurities, were examined using Mössbauer spectroscopy. Three clearly distinct groups of spectral parameters were observed for unused, hydrided and poisoned getter samples. The nature of the getter-deactivation process is discussed, based on these Mössbauer spectral observations. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Inert-atmosphere glove boxes are used to provide secondary containment for most tritium handling operations. For personnel protection and to reduce emissions to the atmosphere, the tritium concentration in the glove boxes is controlled using closed-loop recirculating purification systems. Intermetallic-getter compounds that may be used in these purifiers undergo repeated hydriding–dehydriding cycles during their lifetime, and are often exposed to common atmospheric impurities (O_2, N_2 and water vapour) that enter the glove box through permeation, leakage or accident. Under these conditions, deactivation of the getter and eventual loss of the hydrogen (tritium)-absorption capacity may result. Problems that arise from the interaction of impurities and hydriding–dehydriding cycling usually involve events at the surface. Impurities can interfere with the dissociative chemisorption of hydrogen isotopes on the surface and, depending on the nature of the impurity–getter interaction, impurities can affect hydrogen sorption kinetics, reversible storage capacity, and lifetime of the getters. This paper represents an effort to understand the microscopic reasons for the loss of hydrogen (tritium)-absorption capacity by a common commercial getter, SAES St707 (SAES Getters S.p.A., Via Gallarate 215, 20151 Milan, Italy), consisting of Zr–V–Fe particles [1,2].

Mössbauer absorption of 14.4 keV γ-rays in ^{57}Fe nuclei has been shown to provide useful information on the chemical form of iron in iron-containing hydrogen-getter materials [3,4]. Because getter degradation is expected to influence the chemical form of iron in the getter, the effect of the exposure of impurities on the getter can be monitored by observing the chemical changes in iron. In this study, Mössbauer spectroscopy was used to determine the sensitivity of this technique to monitor the changes in the chemical environment of Fe as a function of exposure of impurities on the commercial getter SAES St707.

2. Experimental

Two different SAES St707 (weight composition ~Zr 70% – V 24.6% – Fe 5.4%) getter samples were examined. One sample, which was deactivated after having been used for approximately 2 years, was obtained from the Chalk River Laboratories tritium-handling glove-box purifier [5]. The other sample was obtained from a fresh batch of the same getter (unused). Initial Mössbauer spectra of these samples were obtained in air-exposed conditions at ambient temperature (in several cases, samples were also examined at liquid nitrogen and liquid helium temperatures), and these results are described in Ref. [5].

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After various treatments, exposure of the getter samples to air for Mössbauer measurements can lead to sample oxidation, thereby complicating the interpretation of the data. Therefore, to avoid exposing the samples to air during the Mössbauer measurements, a special high-temperature, high-vacuum compatible cell was designed and fabricated from quartz. It enabled in situ sample treatment and Mössbauer spectral data acquisition without exposing the sample to air. The absorbers (getter samples) were encapsulated in a fine-mesh nickel screen and held between two stainless steel rings for spectral measurements. With less than 10% absorption of 14.4 keV gamma-rays, such fine nickel screen was found to be suitable for Mössbauer measurements.

The schematic of the experimental set-up is shown in Fig. 1. All measurements were performed using a 50 mCi ^{57}CoRh Mössbauer source. The 14.4 keV gamma-rays were detected with a Kr-CO_2 proportional counter. All specimens were examined at room temperature. The area-based density of the absorbers was between 70 and 120 mg/cm^2. The getter samples were examined after hydriding–dehydriding cycles and after exposure to O_2 and N_2. The used samples were washed with H_2 and degassed under vacuum at 400°C overnight to remove traces of tritium before examination. The fresh getter samples were first activated by vacuum annealing at 400°C (~4 h). Hydrided samples were prepared by filling the sample cell, containing an activated sample, with ultra-high-purity (UHP) hydrogen at 400°C to an initial pressure of ~10 kPa and leaving the sample to equilibrate for ~3 to 4 h. The O_2- and N_2-exposed samples were prepared similarly by filling the sample cell with O_2 or N_2 at 400°C to an initial pressure of ~1 kPa.

The preparation of a sample for in situ Mössbauer measurements was found to be more difficult than expected. Because of the pyrophoric nature of the material, crushing of the unused getter samples in air led to deep oxidation of the samples accompanied by a bright glow. To avoid sample oxidation, a temporary inert-atmosphere box was made to prepare and load the samples into the cell without exposing them to air.

The chemical nature of Fe in various getter samples was determined from the Mössbauer spectral parameters: IS (the isomer shift, which measures the s-electron density at the Fe nuclei), QS (the quadrupole splitting, which measures the electric field gradient at Fe nuclei) and *W* (the line width). Fig. 2 shows examples of the obtained spectra, and Fig. 3 summarizes the results. The main results are given in Table 1.

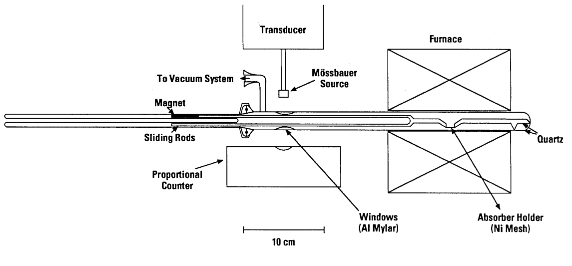

Fig. 1. Schematic of the experimental set-up for in situ high-temperature treatment and Mössbauer transmission measurements.

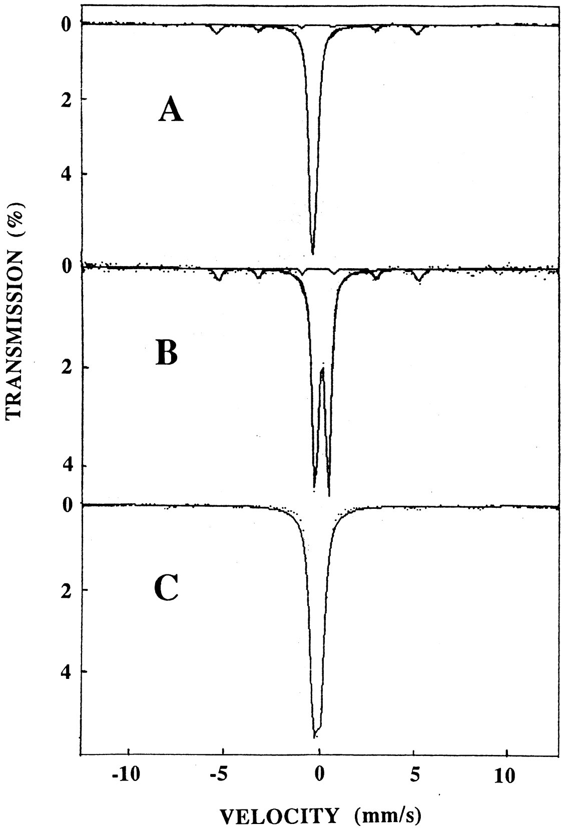

Fig. 2. Representative Mössbauer spectra of getter samples measured at room temperature: A – unused getter, B – hydrided getter, and C – poisoned getter.

3. Discussion of results

The alloy under investigation is multiphase in character, and consisted of a pseudobinary intermetallic Laves-phase compound $Zr(V_{1-x}Fe_x)_2$ ($x \approx 0.17$) with the cubic C15 structure and α-Zr [1]. The metallographic analyses showed that the getter consisted of crystals of $Zr(V_{0.83}Fe_{0.17})_2$ in a matrix of eutectic $Zr(V_{0.83}Fe_{0.17})_2$–Zr. X-ray diffraction analyses of this material showed that the $Zr(V_{0.83}Fe_{0.17})_2$ has a cubic structure C15 with $a = 7.3306$ Å (1 Å = 0.1 nm) in accordance with data from Shaltiel et al. [6]. The $Zr(V_{1-x}Fe_x)_2$ compounds exhibit the cubic C15 structure in the compositions regions $0 \leqslant x \leqslant 0.3$ and

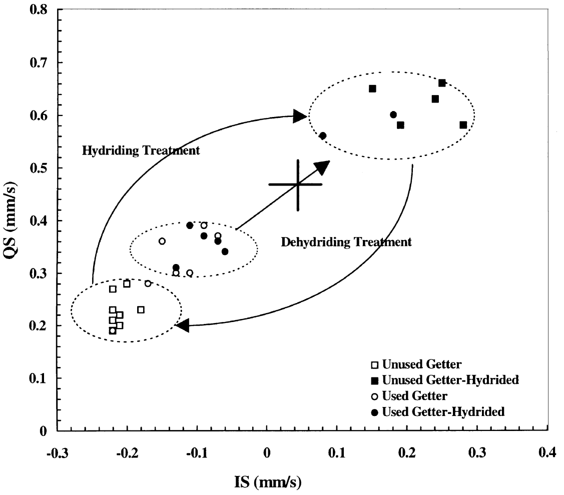

Fig. 3. Correlation of isomer shift (IS) and quadrupole splitting (QS) in getter samples under study.

$0.9 \leqslant x \leqslant 1.0$, and the hexagonal one C14 type in the range $0.3 \leqslant x \leqslant 0.8$ [7,8].

As Fig. 2 shows, the Mössbauer spectrum of the getter sample obtained from a fresh batch (Spectrum A) showed two components: a broad singlet that is due to a $Zr(V,Fe)_2$ Laves-phase with a low Fe content, and a sextuplet that is due to metallic Fe particles (Table 1, Spectra 1-2). The relative spectral area of this metallic Fe component is ~12%. The Mössbauer parameters of the $Zr(V,Fe)_2$ particles observed are consistent with the data for bulk $Zr(V,Fe)_2$ intermetallics [8]. The spectrum of the unused-hydrided sample (Spectrum B, Fig. 2) shows a superposition of a quadrupole doublet, presumably caused by the Zr–V–Fe–H solid solution, and a sextuplet that is due to metallic Fe particles. Used getter samples showed only a broad central line (Spectrum C, Fig. 2), which has been ascribed to the superposition of $Zr(V,Fe)_2$ and $Zr_4Fe_2(O,N)_{0.6}$ components having spectral parameters as given in Ref. [9]. In the limits of experimental resolution, the sextuplets that are due to α-Fe_2O_3 or metallic Fe could not be identified in the spectra of used samples.

Three air-exposed samples (fresh, hydrided and used-hydrided) were reanalyzed using the Mössbauer transmission technique at liquid He temperatures (Table 1, Spectra 15–17). The spectra obtained were similar to those obtained at room temperature. The significantly smaller values of the isomer shift at 4.2 K (see Table 1) were ascribed to the second-order Doppler-shift of the Mössbauer line. Apart from the small magnetically split sextuplet of lines that were due to metallic Fe and α-Fe_2O_3 (observed already at room temperature), the low-temperature spectra did not reveal any other magnetic hyperfine splitting that could be attributed to low-temperature ferromagnetism of the intermetallic component. This finding is consistent with the fact that $Zr(V_{1-x}Fe_x)_2$ Laves-phase intermetallics should become ferromagnetic at 4.2 K only at $x \geqslant 0.5$ [7,8].

The Mössbauer spectra obtained from fresh getter samples from a different batch (Batch 2) were found to differ from Batch 1 (Table 1, Spectra 18–24). The most important observation is the absence of metallic Fe in both the fresh and hydrided samples of Batch 2. As observed earlier, hydriding of the sample led to the appearance of a quadrupole doublet, presumably because of the Zr–V–Fe-hydride solid solution. This process was found to be perfectly reversible with the appearance of the quadrupole doublet that is due to Zr–V–Fe-hydride upon hydriding, which disappeared with the appearance of the singlet that is due to the $Zr(V,Fe)_2$ Laves-phase upon dehydriding. Exposure of this sample to N_2 at 400°C for 1 h did not change the Mössbauer spectral characteristics appreciably. As the data show, the presumably nitrided getter retained the hydriding characteristics to a significant degree, compared with the fresh getter. The nitriding reaction appears to be slow, and under the exposure conditions had only a small effect on the reversible hydriding characteristics of the getter. On the other hand, exposure to O_2 at 1 kPa at 400°C for ~1 h had a significant effect on the reversible hydriding characteristics of the getter, and the damage to the getter appears to be appreciable with O_2.

The absorption of hydrogen isotopes in Zr–V–Fe getters occurs in two steps: (1) dissociation of gaseous hydrogen molecules into atomic hydrogen at the surface of the particles, followed by (2) absorption into the material. The dissociation requires a large energy (~4.5 eV); hence this process is thought to be catalytically assisted, with the Fe metal present on the getter being associated with the catalytically active sites for the dissociation of hydrogen [4]. According to this hypothesis, the gradual loss of gettering activity observed during the glove-box purifier operation may be associated with the loss or conversion of metallic Fe active in the dissociation of hydrogen from the getter, and the irreversible transformation of the intermetallics that are due to exposure of the impurities [5].

Because no metallic Fe was found in the Batch 2 samples, a fresh sample from Batch 1 was re-examined. The data from the Batch 1 samples clearly show the presence of metallic Fe in the getter. Because we have not observed any significant difference in the hydrogen gettering characteristics between different batches of getter, the presence of Fe metallic particles in the getter does not appear to be necessary or crucial for hydrogen gettering.

As Fig. 3 shows, the investigated getter samples fall into three different groups according to their Mössbauer spectral parameters:

Table 1
^{57}Fe Mossbauer parameters of spectra obtained from SAES St707 getter samples

Spec. No.	Sample	Sample (mg/cm^2)	SA (arb.)	IS (mm/s)	QS (mm/s)	*W* (mm/s)	*R* (%)	Identification
Batch 1 – Measured in air at room temperature								
1	Unused	110	0.024	−0.22	0.23	0.40	9	$Zr(Fe,V)_2$, Fe_{metal}
2	Unused	70	0.039	−0.22	0.27	0.38	12	$Zr(Fe,V)_2$, Fe_{metal}
3	Used (from purifier)	110	0.037	−0.15	0.36	0.44	0	$Zr(Fe,V)_2$, $Zr_4Fe_2(O,N)_{0.6}$
4	Used (from purifier)	110	0.025	−0.07	0.37	0.49	0	$Zr(Fe,V)_2$, $Zr_4Fe_2(O,N)_{0.6}$
5	Used (powder – from purifier)	110	0.037	−0.11	0.30	0.45	0	$Zr(Fe,V)_2$, $Zr_4Fe_2(O,N)_{0.6}$
6	Used (pellets – from purifier)	110	0.040	−0.11	0.39	0.48	0	$Zr(Fe,V)_2$, $Zr_4Fe_2(O,N)_{0.6}$
7	Unused/hydrided	110	0.029	0.15	0.65	0.37	12	ZrFeV-Hyd, Fe_{metal}
8	Unused/hydrided	70	0.032	0.25	0.66	0.32	4	ZrFeV-Hyd., α-Fe_2O_3
9	Unused/hydrided	60	0.024	0.28	0.58	0.40	4	ZrFeV-Hyd., α-Fe_2O_3
10	Used (from purifier)/hydrided	110	0.038	−0.09	0.37	0.48	0	$Zr(Fe,V)_2$, $Zr_4Fe_2(O,N)_{0.6}$
11	Used (from purifier)/hydrided	70	0.036	−0.07	0.36	0.45	0	$Zr(Fe,V)_2$, $Zr_4Fe_2(O,N)_{0.6}$
12	Used (from purifier)/hydrided	70	0.040	−0.13	0.31	0.39	0	$Zr(Fe,V)_2$, $Zr_4Fe_2(O,N)_{0.6}$
13	Used (from purifier)/hydrided	60	0.031	−0.06	0.34	0.50	0	$Zr(Fe,V)_2$, $Zr_4Fe_2(O,N)_{0.6}$
14	Unused – CEMS [a]	CEMS [a]	0.003	−0.20	0.28	0.62	0	$Zr(Fe,V)_2$
Measured at liquid He temperature								
15	Unused	110	0.041	−0.07	0.29	0.34	11	$Zr(Fe,V)_2$, Fe_{metal}
16	Unused /hydrided	110	0.052	0.35	0.67	0.50	4	ZrFeV-Hyd, Fe_{metal}
17	Used (from purifier)/hydrided	110	0.049	0.04	0.38	0.50	0	$Zr(Fe,V)_2$, $Zr_4Fe_2(O,N)_{0.6}$
Batch 2 – In situ Treatment and measurements in cell								
18	Unused (dehydrided after 3 hydriding cycles)	125	0.014	−0.21	0.20	0.39	0	$Zr(Fe,V)_2$
19	After hydriding	125	0.013	0.24	0.63	0.39	0	ZrFeV-Hyd.
20	After dehydriding	125	0.009	−0.22	0.19	0.31	0	$Zr(Fe,V)_2$
21	After nitriding	125	0.015	−0.22	0.19	0.31	0	$Zr(Fe,V)_2$
22	After rehydriding	125	0.010	0.18	0.60	0.50	0	ZrFeV-Hyd.
23	After oxidizing	125	0.010	−0.17	0.28	0.53	0	$Zr(Fe,V)_2$
24	Same as above after rehydriding	125	0.011	−0.11	0.39	0.63	0	$Zr_4Fe_2(O,N)_{0.6}$
Batch 1 – New sample								
25	Unused – Measured in air	110	0.036	−0.22	0.21	0.34	11	$Zr(Fe,V)_2$, Fe_{metal}
26	Unused – Measured in air	150	0.030	−0.21	0.22	0.36	13	$Zr(Fe,V)_2$, Fe_{metal}
27	Unused – Measured in cell in air	150	0.010	−0.18	0.23	0.69	3	$Zr(Fe,V)_2$, Fe_{metal}
28	Unused – Measured in cell/hydrided	150	0.006	0.19	0.58	0.51	10	ZrFeV-Hyd., Fe_{metal}
29	Same as above after nitriding	150	0.008	−0.13	0.30	0.47	9	$Zr_4Fe_2(O,N)_{0.6}$, Fe_{metal}
30	Same as above after rehydriding	150	0.007	0.08	0.56	0.53	14	ZrFeV-Hyd., Fe_{metal}

[a] Conversion Electron Mössbauer Spectrum; it measures approximately 300 nm from the top of the specimen surface.

SA is the relative spectral area in arbitrary units, IS is the chemical isomer shift referred to α-Fe at room temperature, QS is the quadrupole splitting, *W* is the absorption line width, and *R* is the fraction of the spectral area ascribed to the Fe_{metal} or α-Fe_2O_3 whichever was identified in the spectrum.

(1) The unhydrided samples that have an IS ranging from −0.15 to −0.25 mm/s and a QS ranging from 0.15 to 0.25 mm/s, whose features can be attributed to $Zr(V,Fe)_2$ C15 type Laves-phase particles.

(2) The hydrided samples that have an IS ranging from 0.20 to 0.30 mm/s and a QS ranging from 60 to 65 mm/s, whose features can be attributed to the Zr–V–Fe-hydride (solid solution) phase. As Fig. 3 shows, the first two states are completely reversible. The profound positive change in IS in hydrided samples might be interpreted in terms of depletion of s-electrons at Fe sites [3].

(3) Completely or partially poisoned getter particles that have an IS ranging from −0.20 to −0.05 mm/s and a QS ranging from 0.30 to 0.40 mm/s. These parameter values can be attributed to either hexagonal C14-type Laves-phase particles or to particles with $Zr_4Fe_2(O,N)_{0.6}$ type cubic structures. Both these possibilities require that a substantial structural transformation of original $Zr(V,Fe)_2$ C15 type particles had to take place during their use. Depending on the extent of the poisoning, these samples can be partially but reversibly hydrided.

According to Pebler and Gulbransen [10], ZrV_2 alloy forms a solid solution with hydrogen without changing its basic structure. The data presented here suggest that $Zr(V,Fe)_2$ particles might have a limited stability on cyclic reaction with hydrogen, especially in the presence of atmospheric impurities. Under these conditions, zirconium hydrides and a zirconium-depleted intermetallic phase may be formed that could favor transformation of cubic $Zr(V,Fe)_2$ C15-type particles to richer in iron hexagonal $Zr(V,Fe)_2$ C14-type particles.

4. Conclusions

This study shows that the Mössbauer spectroscopic technique is sensitive to changes in the chemical environment of Fe in Fe-containing getters and that it can be used as a diagnostic tool to study the effects of cycling and impurity exposure on the hydrogen gettering characteristics, and poisoning of the Fe-containing getters.

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