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Nitriding reactions with a Zr–Mn–Fe metal getter

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Abstract

The metal getter Zr–Mn–Fe (SAES ST909) is an important component of a metal hydride-based tritium clean-up system at Los Alamos National Laboratory (LANL). The system is normally used to clean a glovebox with a helium/nitrogen atmosphere. During start-up operations, it was found that the Zr–Mn–Fe alloy exhibited an anomaly during activation, namely an exotherm upon initial exposure to nitrogen. The purpose of this work is to better understand this nitriding reaction. Nitrogen absorption studies, temperature profile experiments, and powder X-ray diffraction (XRD) were used to study the nitriding reaction. An exothermic reaction between nitrogen and ST909 was observed at ~450°C only when the getter was heated for the first time. ST909 that had been previously heated without nitrogen did not produce an exotherm when heated a second time with nitrogen. Based on the XRD evidence, it was speculated that nitrogen reacts exothermically with the zirconium in the ST909 material. After heating above ~660°C, the aluminum binder in the ST909 melts and may alloy with the zirconium. The resulting alloy appears to be less reactive with nitrogen and does not produce an exotherm. Published by Elsevier Science B.V.

Keywords: Intermetallics; Gas–solid reactions; X-ray diffraction

1. Introduction

Getters are composed of a metal or alloy that can trap particular chemical species. One subset of getters is metal hydrides. Because these materials will selectively remove hydrogen isotopes from a gas stream by forming hydrides, they provide an attractive way to clean-up tritium gas streams [1–4]. Unlike collection on molecular sieve beds, tritium can be trapped with getters without generating tritiated water, which is highly radiotoxic compared to gas phase tritium [1–5]. Furthermore, hydrogen isotopes trapped in a metal hydride getter can be recovered in their elemental form at a later time [4].

Because of their advantages, metal getters have been used in a tritium glovebox clean-up system at Los Alamos National Laboratory (LANL) for several years. One important component of this clean-up system is an ST909 bed, which serves to crack impurities such as Q_2O, CQ_4, and NQ_3 (where Q is any hydrogen isotope) so that the freed hydrogen isotopes can be trapped with a metal hydride getter.

ST909 is composed of equimolar quantities of zirconium (40.5% by weight), iron (25% by weight), manganese (24.5% by weight), and aluminum binder (10% by weight) [6,7]. An ST909 getter bed will crack water with >90% efficiency when operated at temperatures exceeding 400°C and residence times of about 1 s [5]. The atomic oxygen is retained by the getter, but very little of the hydrogen isotopes are absorbed [6–9]. ST909 has also been shown to crack methane, carbon monoxide, and ammonia and retain the atomic carbon and nitrogen [6,10].

The Zr–Mn–Fe alloy exhibits an anomaly during activation, namely an exotherm upon initial exposure to nitrogen. Understanding the source of this exotherm is important in determining the optimal activation conditions for the ST909. The purpose of this work is to characterize the reaction of nitrogen with ST909. Nitrogen absorption measurements were done in order to quantify the amount of nitrogen taken up by the ST909 pellets and to study the kinetics. The phases present in the ST909 material were also studied before and after heating and before and after nitriding with powder X-ray diffraction (XRD) in order to understand changes that occur during activation and exposure to nitrogen. The results are used to suggest a reaction that may be responsible for the exotherm observed during the initial activation of the material.

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2. Experimental

2.1. Nitrogen absorption experiments

Nitrogen absorption experiments were performed in order to quantify the amount of nitrogen absorbed by a known amount of getter material and to study the kinetics of nitrogen absorption. Eight whole or crushed ST909 pellets (~4.8 g) were placed in a 50–70 ml stainless steel sample tube. The sample tube and manifold were evacuated to ~0.7 Pa. Before exposing to nitrogen, the ST909 pellets were activated under active vacuum (~1 Pa) by heating the sample tube to 725°C for 1 h. The sample vessel temperature was regulated with a temperature controller, using a thermocouple as a sensory input. The pellets were then cooled to 675°C and a known volume of high purity (99.999%) nitrogen was delivered by measurement with a calibrated volume. While the temperature was held at 675°C, the drop in manifold pressure was monitored with two capacitance manometers, and the number of moles of nitrogen removed from the gas phase could be calculated at a given time. The number of moles of nitrogen absorbed by the ST909 pellets was equated to the number of moles removed from the gas phase.

2.2. Temperature profile experiments

Temperature profile experiments were done in order to determine at what conditions the exothermic reaction would be observed. The same manifold as described in Section 2.1 was used. Eight whole or crushed ST909 pellets were placed in the sample tube and the manifold was evacuated for about 15 min. The ST909 pellets were then subjected to heating under the controlled conditions listed below:

1. Heat from room temperature to 725°C at ~7°C/min under an active vacuum.
2. Heat from room temperature to 725°C at ~7°C/min under a static vacuum (outgassing not removed).
3. Heat from room temperature to 725°C at ~7°C/min in the presence of high purity nitrogen.
4. Repeat experiments (2) and (3). Before removing the pellets from the sample tube, cool to ~40°C and heat a second time in the presence of high purity nitrogen.

The sample tube temperature was plotted over time. During the reaction, the heat released was great enough that the temperature controller could no longer regulate the sample tube temperature. Therefore, a spike in the temperature profile indicated the presence of the exotherm. It should be noted that the observed exotherm is more significant than the spike in the data would indicate, because the temperature is being measured externally on a sample vessel that is quite massive compared to the ST909 pellets (100 g versus 4.8 g).

2.3. Powder X-ray diffraction (XRD)

ST909 pellets were crushed with a mortar and pestle prior to collecting XRD data. Powder XRD patterns were obtained with a model TED Scintag X-ray Powder Diffractometer with 1.540562 Å X-rays from Cu Kα radiation. The diffractometer was continuously scanned through the two theta range of 20 to 100° with a step size of 0.03 and a scan rate of 0.5°/min. Phases were identified by comparing the peak interplanar spacings (*d*-values) and relative intensities to patterns in the Powder Diffraction Files (PDF) compiled by the JCPDS — International Center for Diffraction Data and previously published Zr–Mn–Fe data [8,11,12].

3. Results and discussion

3.1. Nitrogen absorption experiments

Fig. 1 displays the kinetics of the nitrogen absorption for two different lot numbers of ST909 pellets. Although the kinetics between the two different lots of sample differ substantially, ~0.0028 moles of nitrogen per gram of getter material were finally absorbed in both cases. An elemental analysis of the two different samples by Galbraith Laboratories (Knoxville, TN) for Zr, Mn, Fe, Al, Sn, Cu, V, Ni and Ti showed no significant differences in these two samples and no significant quantities of impurities (<0.1%). Differences in the kinetics may be due to differences in particle sizes. Nitrogen absorption measurements on ST909 samples of different particle sizes are underway.

3.2. Temperature profile experiments

The results of the temperature profile experiments are shown in Figs. 2 and 3. In Fig. 2, the sample tube temperature versus time is plotted for experiments 1, 2 and 3 described in the experimental section. As can be seen, a

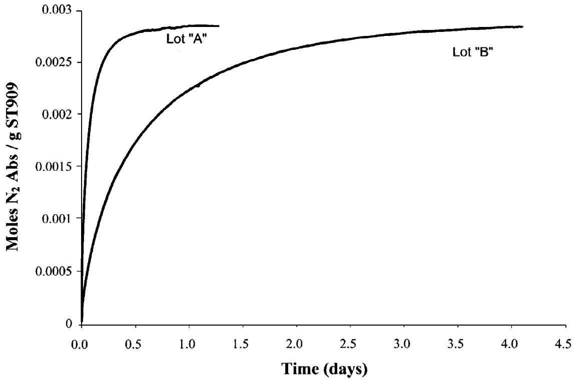

Fig. 1. Moles of nitrogen absorbed per gram of ST909 pellets at 675°C as a function of time. Results from two different lots of sample are shown.

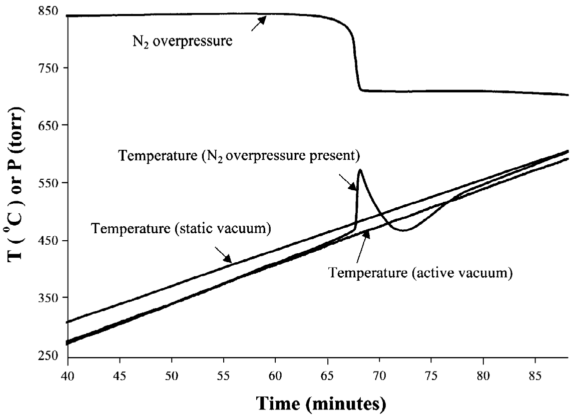

Fig. 2. Results of the temperature profile experiments. The sample tube temperature was plotted as a function of time as ST909 pellets were heated in an active vacuum, in a static vacuum, and in the presence of nitrogen. The manifold pressure (nitrogen overpressure) for the case in which nitrogen was present is also shown.

temperature spike is observed only when the sample is heated in the presence of nitrogen. The manifold pressure is also plotted for the experiment in which nitrogen was introduced before heating (labeled 'nitrogen overpressure'). A large absorption of nitrogen occurs at the same time as the heat release. From this data, we attribute the exotherm to a reaction between nitrogen and the getter or an impurity in the getter. The results of experiment 4 are plotted in Fig. 3. Plot (a) shows the temperature profile of ST909 pellets that were first heated to 725°C without nitrogen, cooled, and reheated to 725°C with nitrogen, and plot (b) shows the corresponding moles of nitrogen that were absorbed. Plot (c) is the temperature profile of ST909 pellets that were heated twice with nitrogen present both times, and plot (d) shows the corresponding moles of nitrogen that were absorbed. Plots (a) and (c) demonstrate that the temperature spike was not observed during the second heating, whether the sample had previously been exposed to nitrogen or not. The temperature spike was not observed at all when the pellets were heated in the absence of nitrogen first as shown in plot (a). This result suggests that the exothermic reaction normally observed during the activation of the ST909 beds can be avoided by heating the pellets to 725°C in vacuum before placing the beds in a nitrogen atmosphere. The second heating cycles in plots (c) and (d) show that a temperature spike need not accompany nitrogen absorption, suggesting two different reactions involving nitrogen. One reaction is exothermic, and can be avoided by heating the pellets in vacuum beforehand as

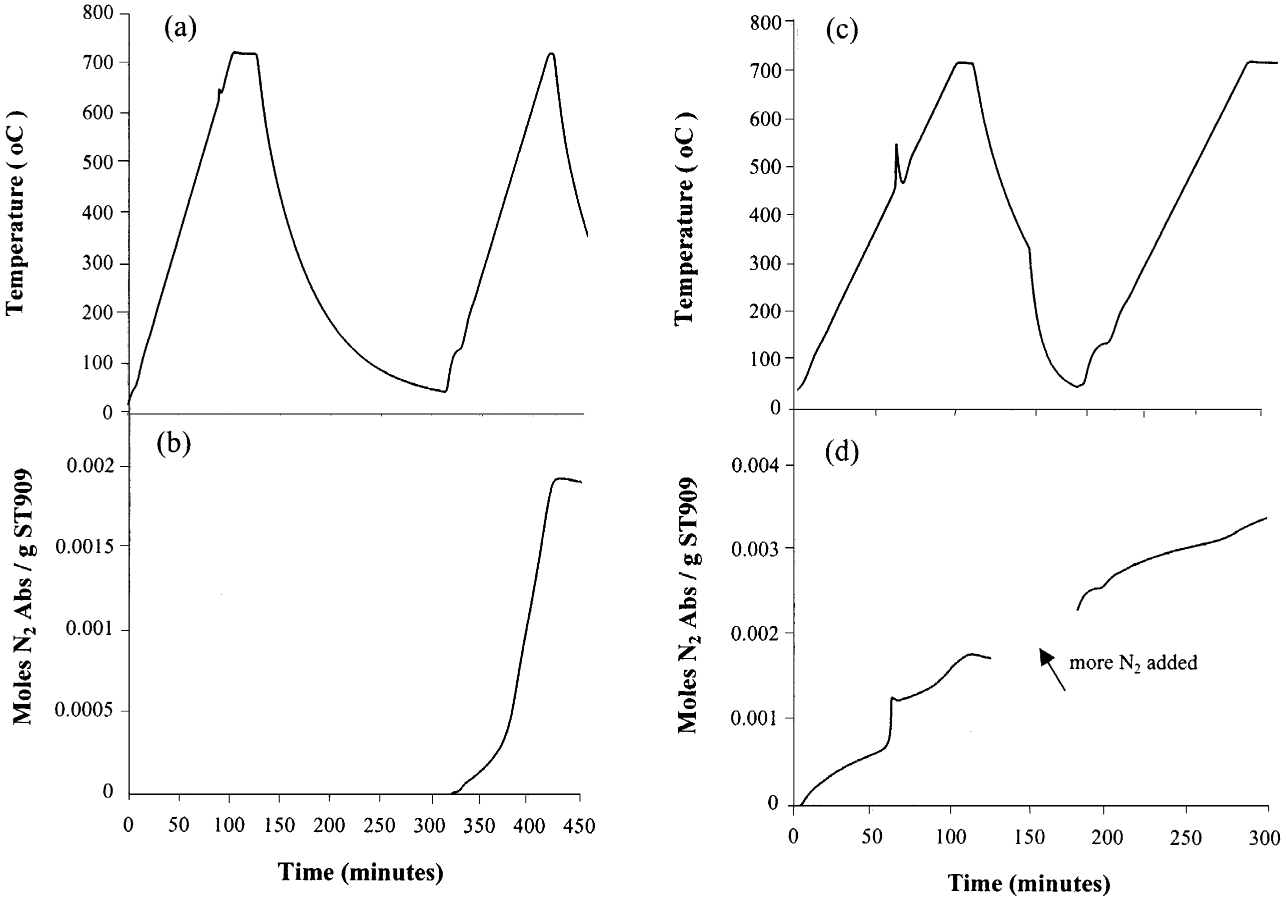

Fig. 3. Sample tube temperatures and corresponding moles of nitrogen absorbed per gram of ST909 as a function of time. Pellets were heated twice under the following conditions: (a) and (b) nitrogen present during second heating cycle only; (b) and (d) nitrogen present during both heating cycles.

described earlier. The second reaction does not produce an exotherm. These experiments were repeated 4–5 times with one lot of ST909. The results were also confirmed with powdered sample of a different lot.

3.3. Powder X-ray diffraction

Fig. 4 shows an expanded region of the XRD patterns obtained from unreacted, heated, and nitrided ST909 pellets. The ‘as received’ pellets produced a pattern containing three phases: Zr–Mn–Fe, Al, and a trace of ZrC. The calculated and observed diffraction pattern of the Zr–Mn–Fe intermetallic compound has been reported [8,11,12], and we observe the same pattern in our data. The presence of aluminum in the diffraction pattern is expected, because aluminum is a binder present in equimolar amounts to the other metals. After heating intact pellets to 725°C for about an hour, the XRD pattern changes somewhat. The Zr–Mn–Fe phase is still present, but the aluminum is gone. Some additional unidentified peaks have appeared, particularly at low diffraction angles. Fig. 4 shows that the aluminum peaks at approximately 38.7° and 44.9° have disappeared in the heated ST909, while unidentified peaks at 38.2°, 44.2° and 45.5° have appeared. Because the melting point of aluminum is 660°C and the aluminum peaks no longer appear in the XRD pattern after the heating step, aluminum likely melts and alloys with one or more of the other ST909 constituents. This new alloy could be responsible for some of the new, unidentified peaks. ST909 pellets that were nitrided resulted in dramatically different XRD patterns as shown in Fig. 4. The hexagonal C14 Zr–Mn–Fe phase is virtually absent from the nitrided sample, and a new pattern that can be attributed to ZrN appears. Other unidentified peaks are also present.

Although we have not been able to identify all of the phases present in the heated or nitrided ST909 samples, we can use the XRD information with the temperature cycling experiments to suggest an explanation for the exothermic reaction. When the ST909 pellets are heated for the first time in the presence of nitrogen, a large release of heat is observed once the pellets reach approximately 450°C. Perhaps the nitrogen is reacting exothermically with the zirconium in the Zr–Mn–Fe phase, resulting in the ZrN phase observed in the XRD patterns of the nitrided samples. If the pellets are initially heated without nitrogen, no exotherm is observed even when the pellets are heated a second time with nitrogen. Perhaps when heating without nitrogen, the aluminum alloys with the zirconium in the Zr–Mn–Fe. It is possible that this new alloy is not as

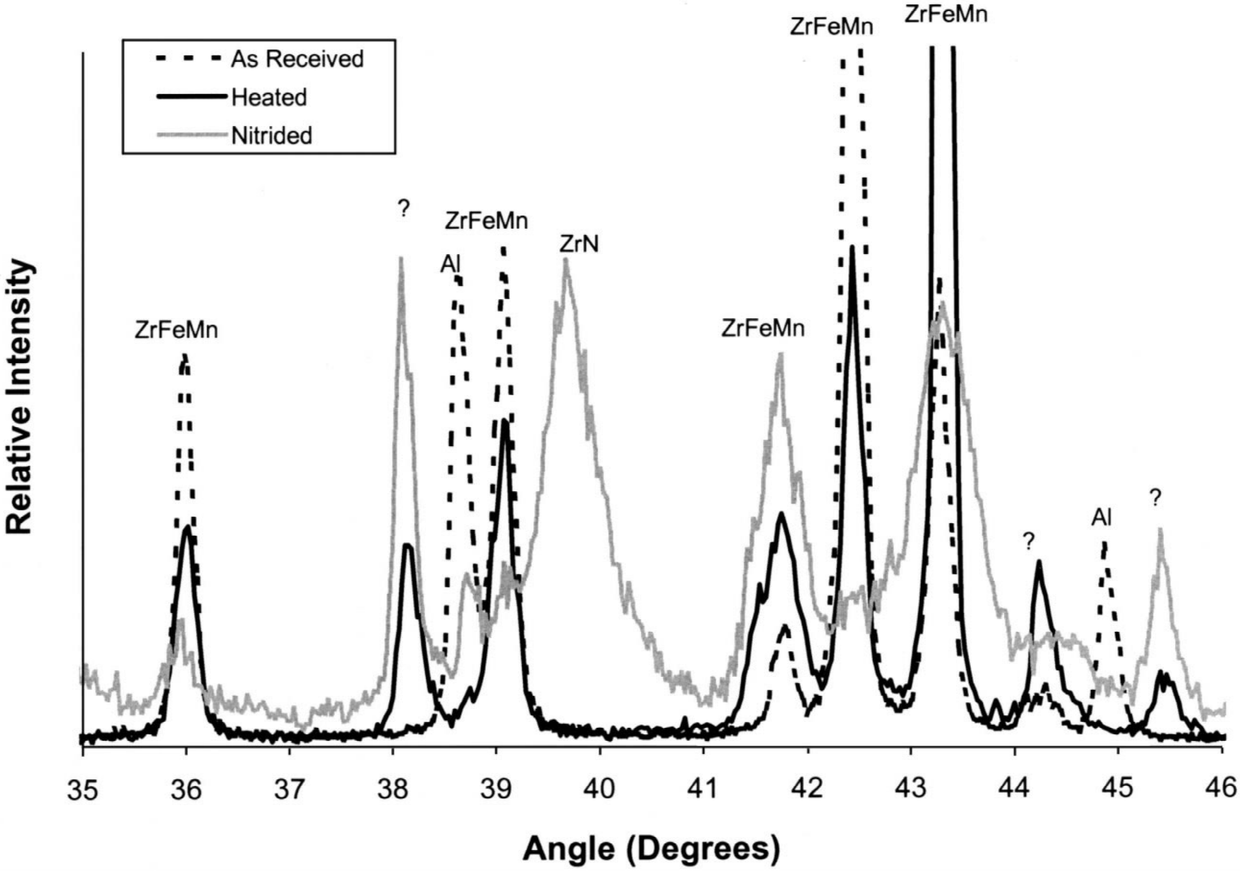

Fig. 4. Portion of the powder XRD data for as received, heated, and nitrided ST909. For display purposes, data were normalized so that the second highest peak in each data set would have a relative intensity of 1.

reactive toward nitrogen and would not produce an observable exotherm upon a second heating with nitrogen.

Unfortunately, we do not have direct evidence to support this explanation, because we have not yet been able to identify the source of all the peaks. We do not know exactly where the aluminum goes after the heating step. The peaks attributed to the ZrN phase in the nitrided XRD pattern are somewhat shifted from the positions recorded in the PDF database, suggesting that the zirconium involved in the nitriding reaction may be alloyed to some other metal like aluminum. There are other experiments that could be performed in order to demonstrate whether or not the proposed explanation is correct. For example, the temperature cycling experiments could be repeated with a mixture of aluminum and zirconium powders to see if an exothermic reaction is also observed during an initial heating in the presence of nitrogen. The phases present in the mixture before and after heating and before and after nitriding could also be studied with XRD to see whether an alumium–zirconium alloys forms after heating to 725°C and to determine which phase absorbs the nitrogen. The XRD patterns would be much simpler and easier to interpret than the patterns associated with the ST909 material.

4. Conclusion

The absorption of nitrogen by the getter material Zr–Mn–Fe (SAES ST909) was characterized by absorption studies, temperature profile experiments, and XRD. An exothermic reaction between nitrogen and the getter material was observed at ~450°C when the ST909 was initially heated in the presence of nitrogen. Heating the getter material in the absence of nitrogen resulted in no observed exotherm even when the sample was heated a second time in nitrogen. It was suggested that nitrogen reacts with the zirconium in the ST909 to produce the exothermic reaction during the initial heating. Heating in the absence of nitrogen may cause the aluminum to melt and alloy with the zirconium, and reduce its reactivity toward the nitrogen. Further experiments to prove or disprove this speculation were proposed. Although the nitrogen-absorbing behavior of the ST909 is still not completely understood, these studies demonstrate that the ST909 getter beds could be heated once in vacuum before being placed on-line in the LANL clean-up system in order to avoid an exothermic reaction when nitrogen is introduced.

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