論　文

Zr-Ni 合金によるメタン分解特性

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Methane Decomposition on Zr-Ni Alloys

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Abstract

Gettering materials are promising for the removal of residual impurities in deuterium-tritium fueled Tokamaks. The decomposition of methane on Zr_7Ni_{10}, ZrNi and Zr_2Ni alloys was investigated in the temperature range from 573 to 773 K. The alloy of Zr_2Ni efficiently removed methane by over 99% in 3 min at 773 K. The pressure decay of methane approximately obeyed the first order kinetics for the three Zr-Ni alloys. The activation energy of the decomposition rate was determined to be 49 kJ／mol for all selected Zr-Ni alloys. The decomposition rate increased gradually, and then, rapidly with the Zr content in the alloys, in contrast to the surface areas decreased from 0.30 m^2／g for Zr_7Ni_{10}, to 0.24 m^2／g for ZrNi and 0.10 m^2／g for Zr_2Ni. The decomposition rate depended also on the surface conditions.

1. Introduction

Gettering materials have been widely applied to tritium processes such as storage, supply, recovery, separation and purification in fusion reactors. The most interesting materials for storage are characterized by very low equilibrium pressure at room temperature and a hydrogen pressure of about 10^3 torr at temperatures below 773 K. For this requirement, uranium beds have been employed as metal tritide interim storage devices[1,2]. However, due to the high chemical reactivity and restrictive use of nuclear materials, alternative getters such as zirconium in pure and alloy forms[3-12] are of interest. The main advantages of Zr alloys include simple activation procedures and low equilibrium pressure for tritium at room temperature, although some improvements are required in the activation temperature, durability against impurities and

deactivation capability.

The most important impurity gases found in various tritium systems are CQ_4, CO, CO_2, O_2, N_2, NQ_3 and Q_2O (Q=H, D, or T). Although equilibrium pressure of tritium at room and about 773 K is a matter of great importance to metal alloys employed for collection and storage of tritium, the influence of reactive impurities on getter performance is also crucial. Penzhorn et al. found that the hydrogen loading capacity of ZrCo progressively decreased as the impurity content increased in the alloy[8, 13]. Thus, both tritium kinetics and capacity are degraded as the carbon, nitrogen and oxygen contents increase in the getter.

Several materials, therefore, have been evaluated for removal of residual impurities in deuterium-tritium fueled tokamaks[4, 13-17]. Wu et al. reported in 1982 that CO adsorbed on Zr-Al alloy at room temperature, but reactivation of the alloy required a heat treatment to 973 K[4]. In their review paper of 1985, Giorgi et al. argued that the hydrocarbons were not usually pumped by getters, but they could be broken down, or cracked by hot filaments or electron currents, and resulting hydrogen removed by sorption[14]. Uranium beds heated to 773, 973 and 1273 K have been found to remove O_2, N_2 and C efficiently[15]. Generally efficient removal was achieved for all impurities except methane which requires 1273 K for efficient cracking. At this temperature, the uranium powder becomes sintered reducing the effective getter surface area of the bed. By using St 909 getter (Zr-Mn-Fe), it has been found that the reactive impurities were efficiently removed from flowing inert gas stream, and removed ratios of about 99% were achieved for NH_3, CO_2 and O_2 at 673 K, CO at 873 K and CH_4 at 973 K[16].

On the other hand, Zr-Ni alloy is one of the promising getters for tritium and vacuum technology, because of its ease in activation, sufficiently low equilibrium pressure of tritium at room temperature, moderate temperature to release tritium gas at one atmospheric pressure and low inflammability against air exposure[5, 7, 12]. In this work, three kinds of Zr-Ni alloys were used to decompose methane in the temperatures range from 573 to 773 K. It is very attractive to remove methane from a vacuum system at lower temperatures.

2. Experimental

2. 1. Materials

Samples were selected from the intermetallic compounds of Zr and Ni. There are eight intermetallic compounds in the Zr-Ni system. In this study, the samples used

were Zr_7Ni_{10}, ZrNi and Zr_2Ni powders with the same weight of 0.5 g. These samples were purchased from Japan Metal & Chemicals Corporation. They were prepared by arc melting method with a high-purity Zr sponge (purity: 99.95%) and Ni blocks (purity: 99.99%), and examined with x-ray diffraction to confirm their structures before use.

2. 2. Apparatus and Procedures

As shown schematically in Fig. 1, the experimental apparatus consists of a vacuum pumping system (RP and TMP), a gas supply system (H_2, Kr and CH_4), a sample tube, a handmade ohm heater and a measure system (mass spectrometer, vacuum gage and pressure gage).

The residual pressure of the vacuum system was usually below 2×10^{-8} torr. The reaction volume was calibrated by gas expansion. Prior to measurements, the sample was activated at 423 K for 2 hours and then at 873 K for 2 hours by a temperature programmer connected to the heater.

Fig. 1. Experimental apparatus used for the investigation of gas/metal reactions.

The surface areas were measured with krypton by the BET method. During the measurements, the sample was cooled with liquid nitrogen. The surface areas were determined to be 0.30, 0.24 and 0.10 m^2/g for Zr_7Ni_{10}, ZrNi and Zr_2Ni, respectively.

The decomposition rate was measured by using the constant volume method with the initial CH_4 of 0.1 torr $\times$ 173 cc, and the exponential pressure decay was monitored with a pressure gage.

3. Results

The behavior of methane decomposition on Zr_7Ni_{10} alloy was examined volumetrically in the temperature range from 623 to 773 K. Very slow cracking of methane was observed to occur on activated Zr_7Ni_{10} alloy at 623 K, leading to a decomposition
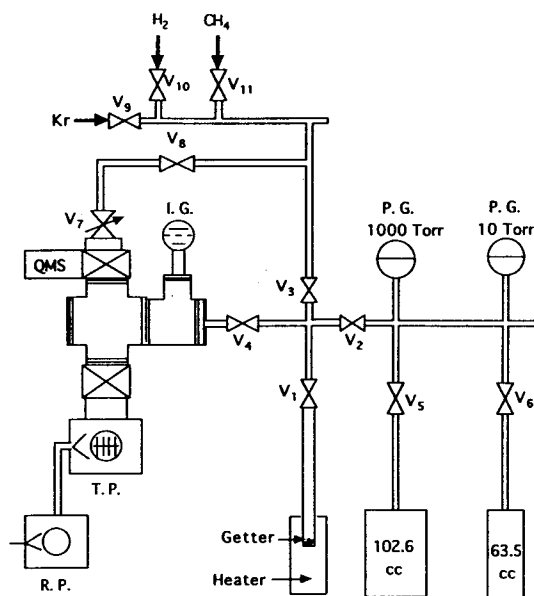
ratio of 1% after 400 seconds. The results of decomposition rates for 673 to 773 K were shown in Fig. 2. The decomposition rate increased rapidly with increasing temperature. In the time of 2000 seconds, about 10% of CH_4 was decomposed at 673 K, while about 50% of CH_4 was done at 773 K.

Figure 3 shows the results of methane decomposition on ZrNi alloy at temperatures of 623, 673, 723 and 773 K. It was seen in this figure that the decomposition rate also became larger as the temperatures increased. In order to achieve the decomposition of 10%, the cracking time of 1800 seconds was required at 673 K. The cracking time, however, reduced to 160 seconds at 773 K for the same decomposition ratio.

The alloy of Zr_2Ni removed methane much more efficiently than Zr_7Ni_{10} and ZrNi alloys. As shown in Fig. 4, this alloy decomposed more than 60% of CH_4 after 2400 seconds even at 573 K, and cracked CH_4 by over 99% in 200 seconds at 773 K. In order to achieve the decomposition ratio of 90% CH_4, this alloy required only 120 se-
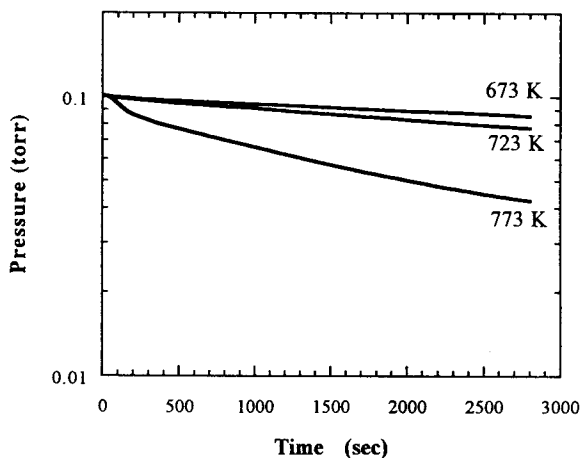

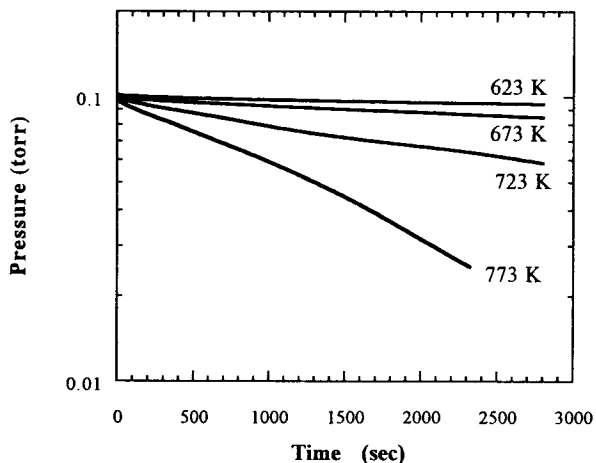Fig. 2. Methane decomposition on Zr_7Ni_{10} alloy.

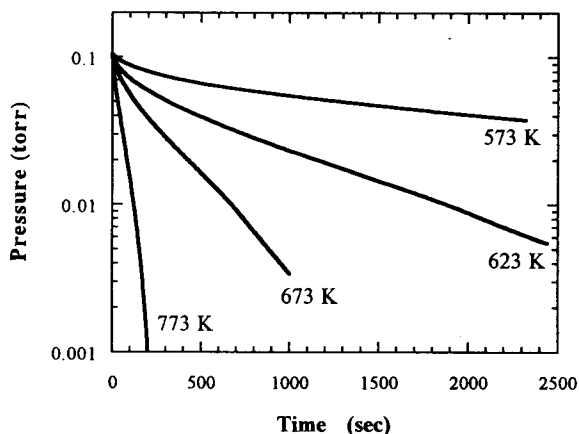Fig. 3. Methane decomposition on ZrNi alloy.

Fig. 4. Methane decomposition on Zr_2Ni alloy.

conds at 773 K, 660 seconds at 673 K and 1860 seconds at 623 K. The alloy is applicable for the removal of residual impurities in deuterium-tritium fueled tokamaks because of the high decomposition rate.

4. Discussion

4. 1. Decomposition temperature

It is much difficult to remove methane among impurities. Its decomposition requires higher temperatures than other impurities. The temperature of a operating purifier is one of the most important consideration, especially in tritium handling applications. Diffusion losses of tritium through purifier walls at high temperatures must be evaluated as it is related to design, safety and accountability.

Zr_2Ni decomposed methane slowly at 573 K and efficiently at 773 K, as shown in Fig. 4. For comparison, the decomposition temperature was listed in Table 1 for some nonevaporable getters. In this table, two temperatures, namely temperature to decompose methane slowly and temperature to decompose methane efficiently were used to characterize methane decomposition on getters.

Methane has been found to decompose slowly on ZrCo powder already at 573 K, a product of 0.05 mol C/mol ZrCo was obtained after about 80 hours when the getter was exposed to 430 torr CH_4[8, 13]. The pumping speeds of Zr-Al for CH_4 and CD_4 have been found to be relatively low and exhibit large temperature dependencies, the pumping speed at 873 K is 20 times larger than that at 650 K[18]. St 707 (Zr-V-Fe) has been reported to be suitable as a methane pump of low speed at low temperatures and pressures after activation in an ultrahigh vacuum system[19]. St 909 getter (Zr-Mn-Fe)[16] and St 198 getter (Zr-Fe)[17] have been found to remove methane efficiently when temperature reaches to 973 K. Uranium requires 1273 K for efficient decomposition of methane[15].

Table 1 Comparison of decomposition temperature for getters

Getter	Temperature to decompose CH₄ slowly (K)	Temperature to decompose CH₄ efficiently (K)	Reference
Zr_2Ni	573	773	this work
ZrCo	573 to 673	–	8, 13
Zr–Al	650	873	18
Zr–V–Fe	673	–	19
Zr–Mn–Fe	–	973	16
Zr–Fe	–	973	17
U	–	1273	15

It is concluded, therefore, that Zr_2Ni is one of the most suitable getters for methane decomposition. The low temperature required for methane decomposition is very attractive in tritium handling applications.

4. 2. Decomposition rate

The pressure decay in Figs. 2 to 4 for the three Zr-Ni alloys approximately follows:

$$dP/dt = kP, \tag{1}$$

where P is the pressure, t the time, and the decomposition rate, k, is given by:

$$k = k_0 \exp\left(-E/RT\right), \tag{2}$$

where E is the activation energy, T the temperature, R the gas constant, and k_0 the pre-exponential factor.

The initial decomposition rate, k_i, was determined from the pressure decay during 0 to 60 seconds. This parameter was employed here to characterize the decomposition rate of methane on gettering materials with clean surface. The temperature dependency of k_i was shown in Fig. 5 for the three alloys.

The activation energy of the decomposition was determined to be 49 kJ/mol for the Zr-Ni alloys. The hydrogen-carbon bond energy for methane has been

Fig. 5. Arrhenius plots of the initial decomposition rates.

reported to be 425 kJ/mol[20] or 406 kJ/mol[21]. Since the dissociation process for methane on Zr-Ni alloys involves breaking bonds in molecules which are also bound to alloy surface, the dissociation energy on the surface would be expected to be much less than the corresponding bond energy of the free molecule. Additionally, this activation energy is also smaller than the surface dissociation energy for methane on Zr-Al alloy, which has been reported to be 59 kJ/mol[18]. This indicates that the decomposition of methane on Zr-Ni alloys is easier than that on the Zr-Al getter.
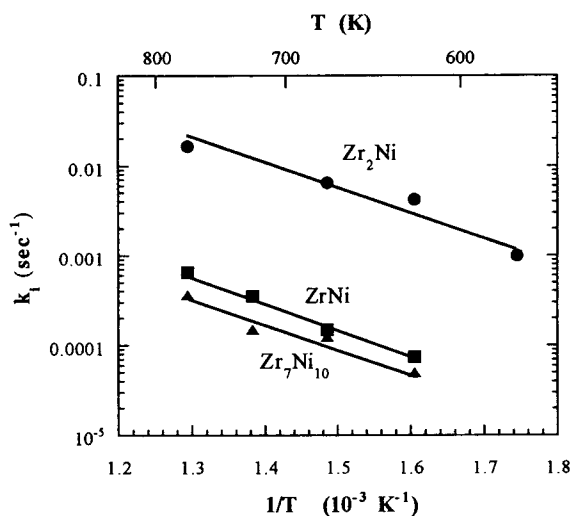
From Fig. 5, it was also seen that same activation energy was obtained for the three Zr-Ni alloys, although there was much difference in the decomposition rates. This suggests that the decomposition is controlled by the same rate- limiting process, either reaction on the getter surface or carbon diffusion in the bulk. The decomposition mechanism remains unclear.

4. 3. Effect of Zr content

The surface areas, A, measured by the BET method were 0.30, 0.24 and 0.10 m^2/g for Zr_7Ni_{10}, ZrNi and Zr_2Ni, respectively. The specific initial decomposition rate, k_i/A, was plotted against the content of zirconium in alloys for the temperatures of 773, 723 and 623 K. As shown in Fig. 6, the specific decomposition rate at each temperature increased gradually and then rapidly with increasing Zr content in the alloys. The results

Fig. 6. The dependence of the specific initial decomposition rates on Zr content in the alloys.

shown in Fig. 6 imply that zirconium in Zr-Ni alloys play key roles in the process of methane decomposition.

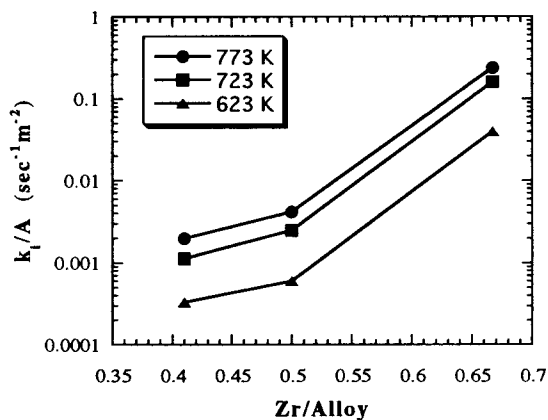This effect seems to arise from either the modification of electronic and geometric structure with the Zr content, or local interactions of methane with nearest-neighbor metal atoms on carbide or hydride formation. It has been reported that carbon on Zr alloys changes its binding state from adsorbed species to carbides and/or contaminant carbon during vacuum heating, and the appearance of metallic Zr on the surface is the principal process for the activation[22]. Further investigations with additional samples, however, are necessary to understand the effect of Zr content on the surface and bulk processes of methane decomposition.

4. 4. Effect of surface activity

The time sequences of methane decomposition on Zr_2Ni at 773 K were shown in Fig. 7 for runs 1, 2 and 3. After run 1, methane was introduced into the sample tube without activation procedure to measure the pressure decay of run 2, and then me-

thane was introduced again for the run of 3.

For run 1, 90% of methane was decomposed in 120 seconds. However, it required 220 seconds for run 2 to decompose 90% of methane, and a longer time (270 seconds) was taken for the run of 3. When the sample was activated at 873 K for 2 hours after these measurements, the pressure decay followed the curve of run 1 again. The results indicated that the decomposition depended on the surface conditions. Carbon on the alloy surface could hinder the following decomposition, and it would diffuse from the surface into the bulk when the sample was heated to higher temperature.

Fig. 7. The time sequences of pressure decay of methane on Zr_2Ni at 773 K for three runs.

5. Conclusions

The decomposition of methane was investigated with three kinds of Zr-Ni alloys. The conclusions of the present study are the following:

(1) The alloy of Zr_2Ni efficiently removed methane by over 99% in three minutes at 773 K. This alloy seems to be one of the most suitable getters for methane decomposition, because of the low temperature required for methane removal.

(2) The pressure decay of methane approximately obeyed the first order kinetics for the three Zr-Ni alloys. The activation energy of the decomposition reaction was 49 kJ ／mol for the alloys, which is smaller than that of Zr-Al alloy.

(3) The specific decomposition rate increased gradually and then rapidly with the increasing Zr content in the alloys. Zirconium in Zr-Ni alloys play key roles in the process of methane decomposition.

(4) The methane decomposition on Zr_2Ni depended also on the surface conditions. Carbon on the alloy surface might hinder the following decomposition, and it could diffuse from the surface into the bulk when the sample was heated to higher temperature.
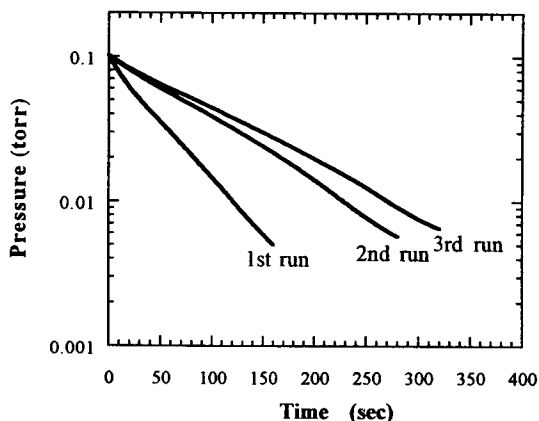
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