Storage of Hydrogen Isotopes on ZrCo and ZrNi

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The CANDU reactors representing a powerful tritium source in time. ICIT Rm. Valcea has developed a technology for the detritiation of the tritiated heavy water based on catalyzed isotopic exchange coupled with cryogenic distillation. Tritium will be removed from the tritiated water and will be necessary for the storage of it in the safe containers. The reference material is uranium because of the high storage capacity and its stability in time, but because of the radioactivity of this material, other material was tested. ZrNi and ZrCo was tested because there are promising materials for storage, supply and recovery of tritium.

Key Words: Intermetallic compounds, Storage, Hydrogen isotopes.

INTRODUCTION

National R and D Institute for Cryogenics and Isotopic Technologies-ICSI Rm. Valcea has a facility for obtaining sorption experimental results of hydrogen and its isotopes on metals and intermetallic compounds *viz.*, ZrCo and ZrNi. These alloys are attractive for tritium storage because of easy to activate, the equilibrium pressure at room temperature is low and for tritium recovery is necessary at moderate temperature.

EXPERIMENTAL

The experimental system for hydrogen isotope sorption are described previously[1].

RESULTS AND DISCUSSION

Before absorption of the hydrogen-tritium mixture, all metal samples were activated in vacuum at 400 °C for 3 h. After activation, the samples were cooled to 25 °C and then were subjected to the process of absorption.

Fig. 1 shows the evolution of temperature and pressure in the system, at the absorption tritium-hydrogen mixture on ZrCo. Reaction begins when solid and gas is in contact, the pressure decreases with increasing temperature and the process is strongly exothermic. Fig. 2 presented the evolution of the hydrogen concentration as time function. For determination of the pressure-composition isotherms, the temperatures maintain at 334, 315 and 296 °C. To obtain each point on the isothermal it
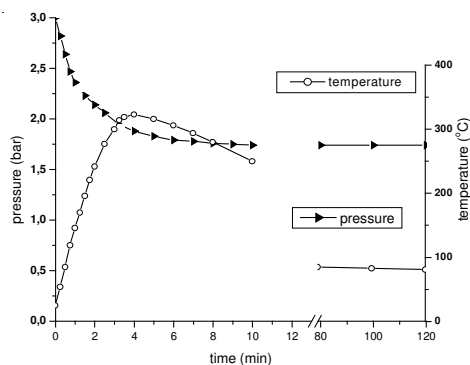
Fig. 1.   Variation of temperature and pressure at the absorption of mixture hydrogen-tritium on ZrCo
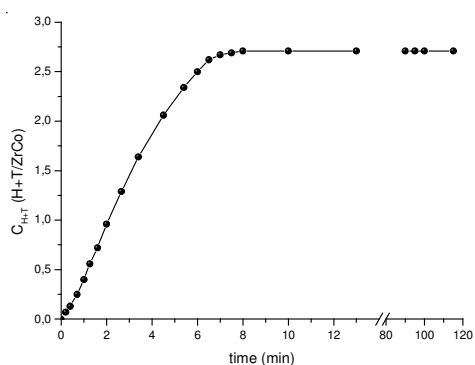
Fig. 2.   Variation of concentration at the absorption of tritium-hydrogen mixture in time on ZrCo

last 5 h. Fig. 3 shows pressure-composition isotherm and noticeable characteristic horizontal area of a constant pressure system formed by ZrCo and hydrogen-tritium mixture. Graphic representation of the logarithm function of pressure in inverse temperature is shown in Fig. 4.
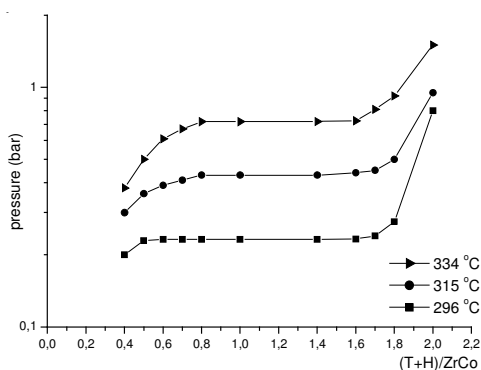
Fig. 3.   Pressure-composition isotherms for tritium-hydrogen mixture absorption on ZrCo
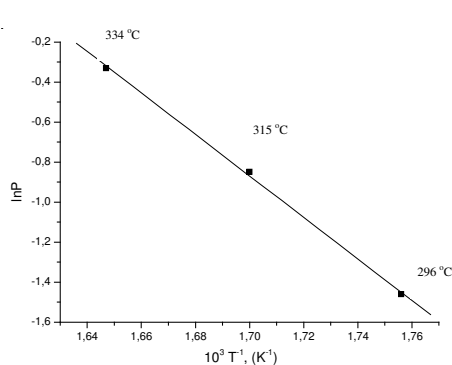
Fig. 4.   Van't Hoff diagram for absorption at hydrogen-tritium mixture on ZrCo

The characteristic of the thermodynamic equilibrium $\alpha \rightleftharpoons \beta$, obtained from van't Hoff representation (Table-1), corresponding compound formation, ZrCoH[2,3].

TABLE-1
THERMODYNAMIC PARAMETERS FOR ABSORPTION
TRITIUM-HYDROGEN MIXTURE ABSORPTION ON ZrCo

ΔH° (kJ/mol)	ΔS° (J/K mol)	Phases in equilibrium
- 86.2	-139.3	$\alpha + \beta$

Fig. 5 presented the variation of concentration (H + T)/ZrNi in time. At the end of reaction, the maximum concentration is 2.61 (H + T)/ZrNi. Fig. 6 illustrated the hydrogen concentration in metal. Temperatures chosen for determining pressure-composition isotherms for ZrNi were lower than those used for ZrCo because equilibrium pressures at high temperatures are high. For example, at 235 ºC, the pressure equilibrium of the system is 1.35 bar and at 200 ºC is 0.74 bar. Each point on the graph of minimum 3 h required for more accurate reading of the pressure equilibrium. Fig. 7 shows pressure-composition isotherms where appears the level characteristic of a constant pressure system formed by ZrNi and hydrogen-tritium mixture. The intermetallic compound ZrNi forms two plateaus of horizontal pressure, the first of them having very low equilibrium pressure[4] (4×10^{-5} bar) and could not be determined experimentally because the equipments could not detect this pressure, even at the temperatures used for determinations. It was obtained only the second level of constant pressure, as seen in Fig. 7.
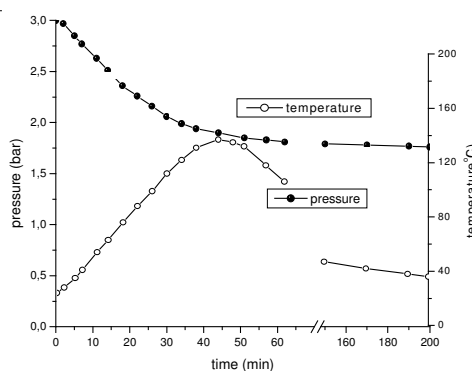

Fig. 5.   Variation of temperature and pressure at the absorption of the hydrogen-tritium mixture on ZrNi
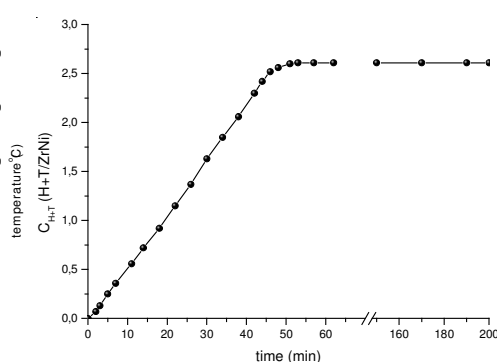
Fig. 6.   Evolution of concentration at the absorption mixture hydrogen-tritium on ZrNi

From graphic representation of a logarithm function of pressure and inverse temperature (Fig. 8), entropy and enthalpy of reaction were calculated corresponding to absorption on intermetallic ZrNi compound. Thermodynamic characteristics are given in Table-2. The values of thermodynamic parameters indicated that tritium stored in ZrNi can be easily recovered by applying a temperature lower than ZrCo.

TABLE-2
THERMODYNAMIC PARAMETERS FOR ABSORPTION
TRITIUM-HYDROGEN MIXTURE ABSORPTION ON ZrNi

ΔH° (kJ/mol)	ΔS° (J/K mol)	Phases in equilibrium
- 35.06	- 71.4	$\beta + \gamma$

Conclusion

The contact between the compound intermetallic ZrCo mixing hydrogen-tritium obtained a concentration of 2.71 (H + T)/ZrCo, were observed constant pressure
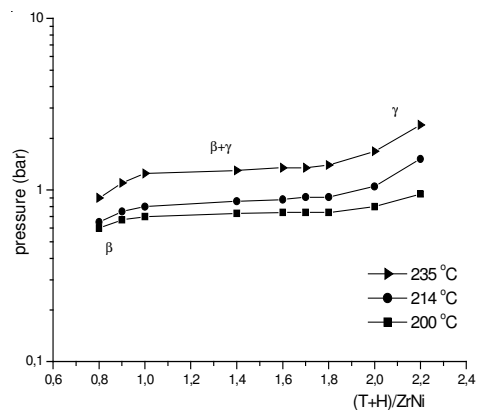
Fig. 7. Pressure-composition isotherms for absorption of tritium-hydrogen mixture on ZrNi
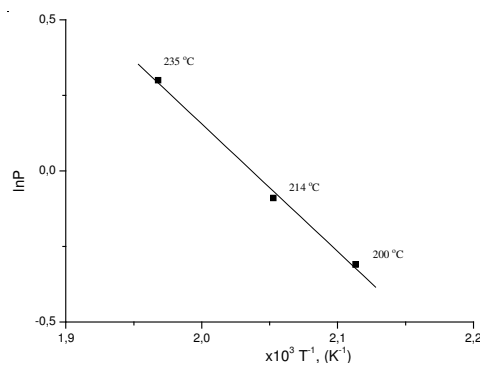

Fig. 8. Van't Hoff diagram for absorption at hydrogen-tritium mixture on ZrNi

level by means of thermodynamic parameters. The value of the enthalpy, determined from the van't Hoff plot, is -86.2 kJ/mol. The reaction is completed in 15 min.

The intermetallic compound ZrNi reacted spontaneously with hydrogen-tritium mixture, the maximum metal concentration was 2.61 (H + T)/ZrNi. The necessary time for obtaining this concentration is 40 min. Enthalpy of reaction (-35.06 kJ/mol) is determined showing stability of hydride formed, lower than ZrCo. From pressure-composition isotherms results, the horizontal pressure plateau is greater than 1 bar at 235 ºC, which leads to the conclusion that the gas stored required lower temperatures for recovery.

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