

Hydrogen extraction from a helium purge gas comparison of the ZrCo/ZAO getter material

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From the known getter materials proposed for the storage, supply, and recovery of hydrogen isotopes the interalloy ZrCo has been selected as reference material. However, because of disproportionation occurring after prolonged thermal cycling, ZrCo loses its ability to reversibly absorb, or desorb tritium. Therefore, several other interalloys such as ZAO have been suggested as potential candidate materials to replace ZrCo. The new materials need to be tested and compared to ZrCo, before their use as replacement to ZrCo. In this report, the same amount (48 g) of both materials (ZrCo and ZAO) are subjected to the same experimental conditions, i.e. to several successive loading-deloding cycles (LDCs) and their performance in terms of absorption/desorption of hydrogen is compared.

This report describes a comparison of the results obtained for both interalloys. It is remarkable to see that although several consecutive LDCs are very similar for ZrCo, this is not the case for ZAO. A constant feature of ZAO is that the first LDC is very different from the subsequent LDCs, since after the first LDC the material does not release the entire amount of hydrogen absorbed during the 1st cycle. This behaviour indicates that for its regeneration, ZAO requires much higher temperatures than the $\sim 430^\circ\text{C}$ used here, although 430°C is enough to regenerate ZrCo. Furthermore, the formation of several hydrogenated species involving some other ZAO's constituents (V, Ti, etc...) could also explain the need for a higher regeneration temperature, some of them are assumed to have different activation energies for the hydrogen release and therefore require higher regeneration temperatures.

1. Introduction

From the known getter materials proposed for the storage, supply, and recovery of hydrogen isotopes, the interalloy ZrCo has been selected as the reference material. However, because of disproportionation occurring after prolonged thermal cycling, ZrCo loses its ability to reversibly absorb, or desorb tritium. Therefore, several other interalloys such as ZAO have been suggested as potential candidate materials to replace ZrCo. The new materials need to be tested and compared to ZrCo, before their use as replacement to ZrCo. In this report, the same amount of both materials (ZrCo and ZAO) are subjected to exactly the same experimental conditions, i.e. to several successive loading-deloding cycles (LDCs) and their performance in terms of absorption/desorption of hydrogen is compared.

The experiments have been carried out at the Tritium Laboratory Karlsruhe (TLK), using the HYdrogen-DEuterium (HYDE) loop.

The present work is not intending to investigate the loading and deloding capabilities of both getter materials from a kinetic and/or

thermodynamic point of view, this has been done elsewhere [1,2] but it is rather focused on a comparative evaluation of their respective behaviour toward H_2 absorption and desorption.

Moreover, extensive studies on hydrogen isotope storage behavior of ZrCo [3–9] have been carried out by many investigators, since ZrCo is considered as the reference candidate material for ITER-SDS [3,4,6–8]. The reason is that ZrCo has several advantages over the Uranium such as; it is non-radioactive, non-pyrophoric at room temperature and has similar tritium storage properties as uranium.

On the other hand, ZAO is a relatively new compound and there is not much information in the literature [9,10]. Therefore, it seems appropriate to compare the loading/deloding capabilities of the ZAO material with the current reference material, i.e. ZrCo.

In this regard, five consecutive LDCs have been carried out using 48 g of ZrCo or ZAO. During the loading phase, the getter bed was purged with a constant flow of He and H_2 with an H_2/He ratio of approximately 0.003. During this series of experiments, the experimental parameters such as the getter bed temperature, pressure drop and He and hydrogen

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flow rates have been recorded and the results analysed.

This report describes a comparison of the results obtained for both interalloys. It is remarkable to see that although all consecutive LDCs are very similar for ZrCo, this is not the case for ZAO. A constant feature of ZAO is that the first loading/deloading cycle is very different from the subsequent LDCs. The reason lies with the fact that after the first loading ZAO does not release the entire amount of hydrogen absorbed during the first cycle.

2. Experimental

ZrCo and ZAO® samples were provided by SAES Getters, Milano, Italy. Usually, the material is presented as ingots; however, both materials delivered by SAES were a granular conglomeration of particles with an average size ranging from 1 to 6 mm. (Fig. 1).

It is worth noting that ZAO® is not an abbreviation but a brand name given by SAES to an interalloy made out of <80 % Zr, <20 % Al but also containing V, and Ti [9].

Before the material is submitted to hydrogen exposure, it is important to activate it. Activation is done in two steps/phases. During the first phase, the getter was heated up to ~430°C under vacuum for about 8 h. This process was repeated. During this first phase, it was noticed that in addition to water and oxygen, the material was also releasing some hydrogen. We assumed that the material had been previously submitted to some LDCs performed by the manufacturer.

In general, the activation process involves exposing the material to a reactive gas, such as hydrogen. Therefore, during the 2nd phase of the activation process, the material is exposed to pure hydrogen for a couple of loadings. This final step allows the material to crack into very fine grains and increases the surface of absorption.

During the regeneration (H₂ deloading phase) the resulting internal stressing produced by the hydrogen release, leads to the grain cracking and cracking of the crystal structure of the hydride, thus reducing the size of each particle. This phenomenon is known as hydrogen decrepitation.

2.1. The HYDE loop

For these tests we used the HYdrogen-DEuterium (HYDE) loop located at the Tritium Laboratory Karlsruhe (TLK) at KIT.

Originally, the HYDE loop was designed with the aim of providing H₂/D₂ mixtures for calibrating analytical devices such as gas chromatographs and laser Raman spectroscopy. However, it was upgraded to allow us to perform the needed measurements with the getter bed. The Pipe and Instrumentation Diagram (PID) of the HYDE loop is illustrated in Fig. 2.

During the loading (adsorption) phase, the experiments are performed in a closed loop (to save cost for He while operating at relatively high flows):

- The loop is filled with He that is being recirculated at relatively high flow rates,



Fig. 1. ZAO® and ZrCo raw materials.

- Then H₂ is added upstream of the getter bed at a given and fixed flow rate,
- The mass spectrometer placed downstream of the ZrCo bed, is monitoring the whole process giving measurements H₂ and He exiting the getter bed.
- The experiment is carried out until a breakthrough is reached. At that moment, H₂ concentration starts to rise (H₂ is not any longer absorbed by ZrCo).

Mirz et al. [11] have reported a detailed description of the whole system and procedure.

2.2. The getter bed

The central part of this set-up is the getter bed which receives the getter material (either ZrCo or ZAO).

The CAD of the new getter bed is shown in Fig. 3. The getter bed consists of a AISI 316 L stainless steel tube, which is enclosed between two DN40CF flanges. AISI 316 L stainless steel is a molybdenum-alloyed austenitic chromium-nickel steel, allowing improved machinability.

As it is illustrated in Fig. 3, the reaction chamber is divided into 6 separated compartments. This allows the segregation of the material in order to avoid its conglomeration due to the material expansion after it is loaded with hydrogen. This would be especially detrimental when the bed is fully loaded with getter material (ZrCo or ZAO), as hydrogenation leads to an expansion of the crystal lattice by about 20 % [12].

Each compartment is loaded with the same amount of getter material. For the experiments using 48 g of getter material (ZrCo or ZAO), each compartment was filled with 8 g of material. When fully loaded, the getter bed can be filled up with up to ~300 g of ZrCo, or approximately 245 g of ZAO. It must be noted that for the same available volume the getter bed can accommodate more ZrCo than ZAO, since the latter is lighter having a lower density. The estimated density for ZAO is $6.0 \pm 0.2 \text{ g/cm}^3$ whereas for ZrCo the density is 7.7 g/cm^3 .

It should also be noted that the size reduction of the material due to hydrogen decrepitation can lead to the formation of very fine particles, or dust. Fine dust particles have an average size ranging between 1 and 10 μm whereas ultrafine dust has sub-micrometre dimensions. Obviously, the smaller the grain size, the easier it is to be carried away by the purge gas, even outside the getter bed and hence contaminate the whole experimental setup. Working with H₂ or D₂, this is not a major issue, but it becomes hugely problematic when working with tritium. In our current getter bed design, to prevent the powdered dusty material from exiting the getter bed, each compartment of the getter bed was equipped with a 1 mm thick SiperM R3 sintered 316 L stainless steel disk.

The SiperM R3 disks are porous with an average pore size of 2.8 μm and mitigate the transport of the finest particle grains to the rest of the equipment. We found that R3 SiperM disks offer the best compromise between small pore dimensions without affecting much the pressure drop resulting by the reduction of the pore size. Furthermore, at the end of each side of the bed, a 1 mm thick SiperM R3 disk was also welded onto the tube [see ref. 11].

2.3. Loading-deloading experiments with 48 g of ZrCo

The getter bed is filled to 16 % of its maximum capacity.

For the loading experiments with ZrCo, the experimental conditions are reported in the Table 1 below.

During adsorption phase, the experiments are performed in a closed loop :

- The loop is filled with He that is recirculated at relatively high flow rates (~ 16 NL/min),
- Then H₂ is added upstream of the getter bed at a given and fixed flow rate (~50 Ncm³/min),

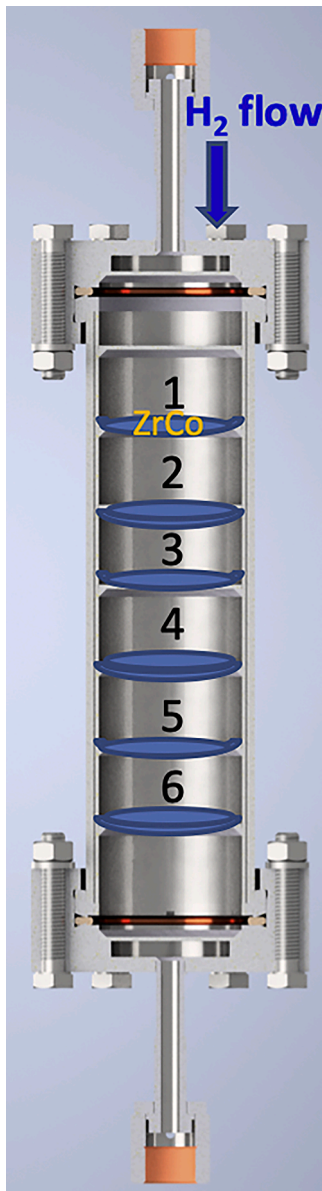


Fig. 3. CAD of the getter as in operation, illustrating the six compartments (right).

Table 1
Experimental parameters for the loading of ZrCo.

Sample	ZrCo
Mol. Weight (g/mol)	150.16
Mass (g)	48 (0.32 mol)
Hydrogenated Compound	ZrCoH ₃
Max. Theor. Absorbed H ₂ (NL)	11.6
Max. Theor. Hydrogen Absorbed (NL/g)	0.24
He flow rate (NL/min)	16.2 ± 0.3
H ₂ Flow Rate (Ncm ³ /min)	50
Pressure (mbar)	1000–1100
H ₂ /He	~0.31 %

The first loading cycle is illustrated in Figs. 6 & 7.

As can be seen, the loading process is very similar to that observed for ZrCo.

When comparing the corresponding figures for the pressure drop, we may notice that for the first loading cycle of ZAO, the pressure drop is approximately the same as the one observed for ZrCo. This is normal as

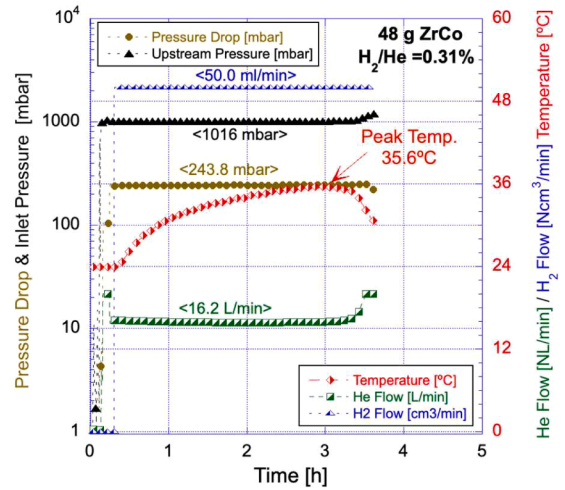


Fig. 4. Typical parameters for ZrCo loading.

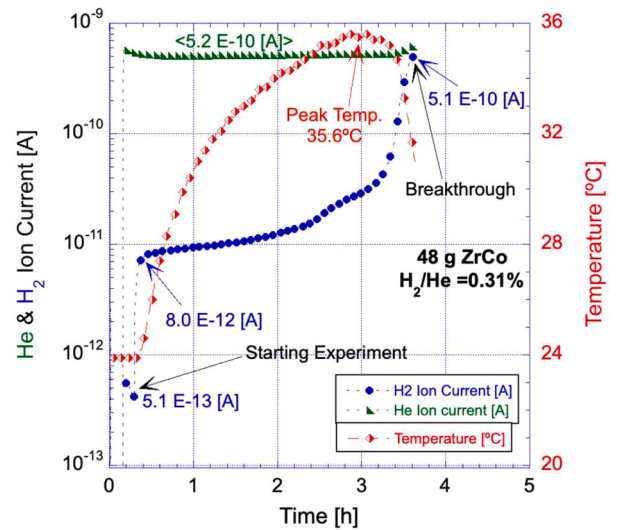


Fig. 5. QMS spectrum for the H₂ and He currents (log scale) obtained for ZrCo loading.

Table 2
Summary of the loading experiments of 48 g ZrCo.

Loading Cycle	He / H ₂ flow rate	H ₂ /He [%]	Aver. Press. Drop [mbar]	Peak Temp. [°C]	Time to reach Peak Max. Temp. [h]	Abs. H ₂ [NL]	H ₂ fract. In ZrCoH _x
1	322	0.31	232.0	33.9	2.2	9.6	2.5
2	319	0.31	243.8	35.6	2.7	10.9	2.8
3	325	0.31	231.5	35.2	2.4	11.1	2.9
4	324	0.31	232.4	35.1	2.6	11.4	2.9
5	324	0.31	233.8	35.1	2.4	11.1	2.9
Average	322.8	0.31	234.7	35.0	2.5	10.8	2.8

the principal factor of the pressure drop, is the getter bed itself.

From the Quadrupole Mass Spectrometer (QMS) spectrum we can make similar observations to the ones described above for ZrCo. The whole process discussed above is illustrated in Fig. 7.

As one can see, at the beginning of the experiment (bypassing the getter bed), the H₂ signal is very low, i.e. 2.3 E-14 A (background level).

Table 3
Experimental parameters for the loading of ZAO.

Sample	ZAO
Mol. Weight (unknown)	-
Mass (g)	48
Hydrogenated Compound	ZAOH _x
Theor. Max. Absorbed H ₂	Unknown
He flow rate (NL/min)	15.4–16.8
H ₂ flow rate (Ncm ³ /min)	50
Pressure (mbar)	1000–1100
H ₂ /He	~0.32 %

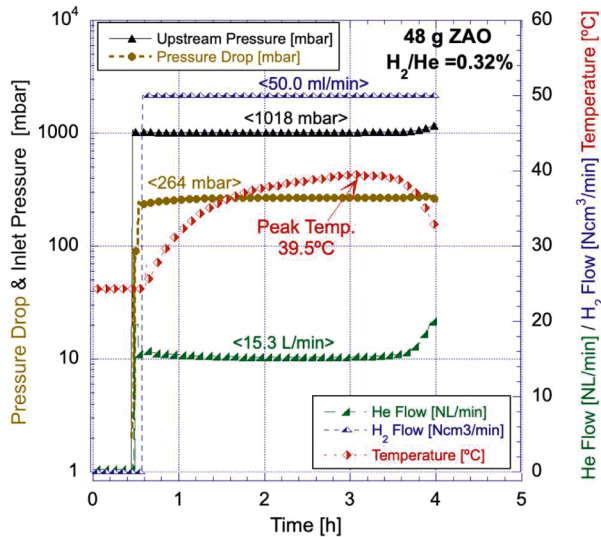


Fig. 6. He and H₂ flow rates versus temperature during the first loading of ZAO.

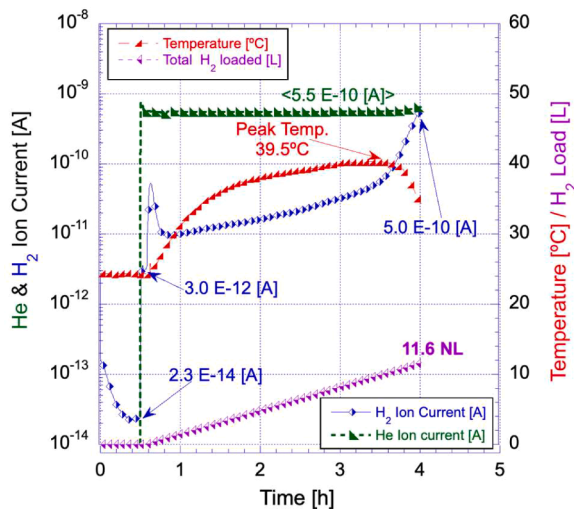


Fig. 7. Experimental QMS parameters recorded during the first load of 48 g of ZAO.

However, by allowing H₂ to cross the getter bed, its level increased immediately to 3.0 E- 12 A, although H₂ is now starting to be absorbed by the getter material. As the experiment is progressing, the H₂ signal is continuously increasing gradually until the ZAO is “filled up” (saturated) with H₂, and thus more and more hydrogen escapes the getter bed and finally reaches the point where the H₂ signal reaches almost the He level (5.0 E-10 A). On the other hand, during the whole experiment the He signal remains remarkably constant (5.5 E-10 A). This is normal since

He crosses the bed without any interaction.

Table 4 summarises the results obtained for the 5 successive loadings of ZAO.

What stands out when looking to these results, is the difference between the first loading and the subsequent loadings of ZAO.

It is remarkable to see that during the first loading about 11.6 NL hydrogen is trapped by the getter material, but during the deloading less than half of it is released. Obviously, the deloading process does not release the whole amount of trapped hydrogen. It follows that the deloading temperature at ~430°C was not high enough to fully deload ZAO, although 430°C is sufficient to fully deload ZrCo. As we do not know the exact chemical composition of the ZAO material (besides the fact that it is an interalloy which is containing Zr, Al and Ti), since the manufacturer did not disclose its chemical composition, it is assumed that the hydrogenation process generates various types of hydrogenated alloys, such as TiH₂, or VaTiH_x, which have different activation energies for the hydrogen release and thus different releasing temperatures. Therefore, a much higher temperature is required to fully deload the ZAO-hydride.

It is beyond the scope of this report to investigate the thermal behaviour of ZAO hydride; however, before using it as a potential replacement for ZrCo, it is mandatory to perform a thorough thermal analysis to investigate at what temperature the hydrogen release of the ZAO material will be quantitative.

After the first loading the subsequent LDCs show an almost similar pattern. It is also worth noting that after the first loading, the absorption capabilities of the material have been decreased, since all H₂ has not been released after the first deloading. We may also note that the total amount of hydrogen trapped by the getter is steadily decreasing, cycle after cycle. The last column of Table 4 is illustrating that, where is reported the percentage of hydrogen trapped by the material after each loading cycle, in comparison to the first loading.

A full report for the 5 consecutives cycles for both materials (ZrCo & ZAO), including their behaviour during the desorption phase, has been published elsewhere [13].

3. Conclusions

Hydrogen getter materials are of potential interest for the handling, transport and storage of tritium. Amongst them, ZrCo is considered as the reference candidate material for ITER-SDS. However, because of the disproportionation occurring after prolonged thermal cycling, ZrCo loses its ability to reversibly absorb or desorb tritium. Therefore, several other interalloys such as ZAO have been suggested as potential candidate materials to replace ZrCo. In order to evaluate the performance of the ZAO getter against repetitive LDC, ZAO needs to be tested and

Table 4
Summary of the loading experiments of 48 g ZAO.

Loading Cycle	He / H ₂ flow rate	H ₂ /He	Aver. Press. Drop	Peak Temp.	Time to reach Peak Max. Temp.	Abs. H ₂ [NL]	H ₂ fract. in ZAOH _x (%) [#]
		[%]	[mbar]	[°C]	[h]	[NL]	(%) [#]
1	306	0.32	264.4	39.5	2.6	11.6	100
2	307	0.30	263.7	34.6	1.1	5.7	49.1
3	314	0.32	263.9	30.1	1.1	4.9	42.2
4	313	0.32	255.3	35.5	1.2	4.5	38.8
5	315	0.32	254.3	33.5	1.3	4.3	37.1
6	314	0.32	254.3	34.3	1.4	4.8	41.4
7	312	0.32	259.0	33.1	1.4	4.6	39.7
Average	312.5	0.32	258.4 ± 5.2	33.5	1.25	4.9 ± 0.5	41.4 ± 4.2 [*]

[#] The percentage is expressed in comparison to the first loading.

^{*} Average not taking into account the first loading.

compared to ZrCo. This report describes the preliminary investigation testing both getters under the same experimental conditions using the same amount of material (48 g).

During the test, the experimental parameters such as the bed temperature, the pressure drop, and He and hydrogen flow rates were recorded and the observed results are described below.

ZrCo. For the experiments using ZrCo, 2.5 h were needed to reach the maximum temperature peak, which corresponds to the hydrogenation of the sample (ZrCoH_3) and approximately another 30 min for the full load of the getter material.

The ZrCo could not be loaded at 100 % (ZrCoH_3) and therefore the maximum theoretical fraction ($x = 3$) was never reached. However, the material was fully deloaded after each bed regeneration and the entire hydrogen fraction trapped by the material was released with an average hydrogen fraction $x = 2.8$, which corresponds to a hydrogen absorption of ~ 10.8 NL.

ZAO. The experiments using ZAO showed a big difference between the first loading and the subsequent loadings. During the second loading, the sample could absorb less than 50 % hydrogen compared to the first loading. Moreover, during the following loading the material exhibited a similar pattern.

It is also remarkable to see that during the first loading more than 11.6 NL hydrogen was trapped by the getter material, but after regeneration only half of it was released. For the second loading, only 5.7 NL H_2 is trapped and during the subsequent cycles this amount is even lower averaging ~ 4.9 NL H_2 for the four loadings. This behaviour indicates that for its regeneration ZAO requires much higher temperatures than the $\sim 430^\circ\text{C}$ used here, although 430°C is enough to regenerate ZrCo. Furthermore, it was also assumed that the possible formation of hydrogenated species, such as TiH_2 , or VaTiH_x , could also explain this difference in regeneration temperature, since some of them have higher activation energies for the hydrogen release. It is therefore, suggested to conduct a thorough thermal analysis of ZAO hydride, in order to investigate its hydrogen release against temperature.

Finally regarding the pressure drop, it must be noted that the principal factor of the pressure drop is the getter bed itself. The larger volume of ZAO in comparison to the volume occupied by the same amount of ZrCo does not seem to affect that much the pressure drop as only 48 g of material was used. But this could become more important as we fill the getter bed to its maximum capacity.

CRedit authorship contribution statement

N. Bekris: Writing – original draft, Writing – review & editing. **M. Sirch:** Investigation. **I. Cristescu:** Project administration. **R. Groessle:** Resources.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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