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Intermetallic alloys as hydrogen getters

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Abstract

Metal hydrides were discovered in the fifties and since then have been widely studied and developed, mainly for energy applications (batteries, hydrogen storage, compression...). In addition to these uses, other properties are considered such as sensors, actuators, or scavengers. This paper proposes a review of intermetallic-based materials for hydrogen gettering. The different chemistries (Zr- or Ti-based compounds) are described in terms of alloying elements and gettering properties. Various aspects, including the activation process, surface coating and resistance to impurities, are also discussed. Finally, new processes and other possible applications are discussed for these materials.

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Introduction

Dihydrogen is nowadays considered as a promising energy carrier and lot of efforts are done worldwide to develop its production, storage, and conversion for a clean energy market. However, hydrogen gas can be also seen as a hazardous molecule leading to embrittlement of steel, radioactivity with its isotope tritium, explosive atmosphere if mixed with stoichiometric oxygen or a troublesome residue in ultra-high vacuum (UHV) technologies. Therefore, in addition to energy applications, research is being conducted to mitigate the risks and safely handle this industrial product.

Dihydrogen handling can be done by using various materials able to trap the gas safely in solid state. In the 70s, Sandia National Laboratories developed organic scavengers based on 1,6-diphenoxy-2,4-hexadiyne (DPPE) [1], 1,4-bis(phenyl ethynyl)benzene (DEB) [2,3] and 1,4-diphenylbutadiyne (DPB) [4,5], all reacting with hydrogen gas [6]. The hydrogenation of the carbon-carbon double or triple bonds of these materials requires the intervention of catalysts such as platinum and palladium and different supports such as graphite, aluminum oxide or barium carbonate, which can represent up to 25% by mass of the scavenger. Many organic scavenger/catalyst combinations have been patented in this field [7,8].

Beside organic materials, mineral oxides have also been considered as hydrogen absorbers [9,10]. The thermal and chemical stability and the resistance to irradiation of these materials allow their use as irreversible traps. Among them, various manganese oxide-based mixtures have been studied [11–13]. Galliez determined that, among the different polymorphic varieties of manganese oxides, *nsutite* has the best H₂ trapping kinetics [14]. Several other mixtures have been considered for H₂ chemisorption such as MnO₂/Ag₂O, calcium oxide and cobalt oxide. They are produced by the company SAES Getters under the name Combogetters [15]. They also contain a barium-lithium alloy to adsorb impurity gases (N₂, O₂ and CO₂). Whatever the proposed oxide mixture, a catalyst is needed to increase the trapping capacity of the mineral oxides. These catalysts are generally metal oxides such as palladium oxide or transition metal oxides [16] for which the presence of moisture, CO or HCl are prohibitive [15].

The last category of scavengers are hydride-forming alloys. Those materials can chemisorb hydrogen in a very wide range of temperatures and pressures, including alloys with very low

equilibrium pressures to ensure irreversible hydrogen trapping. A few getters have been developed using pure elements like titanium, zirconium, or even depleted uranium. However, most of the hydrogen scavengers are multi-elementary compounds and these alloys are known as Non-Evaporable Getters (NEG) [17]. They allow, among other purposes, to reach ultra-high vacuum conditions in synchrotron facilities [18] and micro-electro-mechanical systems (MEMS) [19] or the recovery of tritium in nuclear applications (like ITER) [20–22]. However, though these materials can react spontaneously with hydrogen and trapping it at very low pressure [23], the reaction with the bulk requires a preliminary surface dissociation step that can be strongly affected by either the possibly oxidized surface state or by the gas composition (if not pure hydrogen) in the presence of molecules such as moisture, O₂, SO₂ or CO [24]. A schematic view of the process is shown in *Figure 1*.

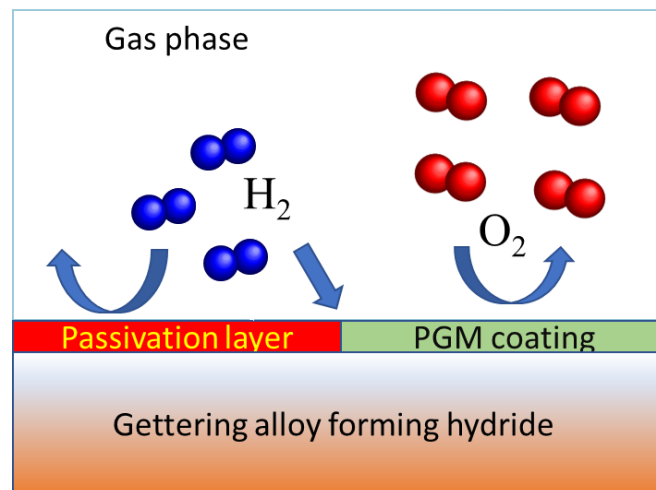


Figure 1 – Schematic view showing a gettering alloy forming hydride at low equilibrium pressure. Hydrogen molecules from the gas phase should first adsorb at the surface before dissociation and diffusion into the bulk. Surface can be passivated by other species present in the gas phase (like oxygen) needing an activation treatment (red part) or protected by a film of noble metals (Platinum group metal PGM; green part).

The purpose of this article is to review the intermetallic compounds that have been developed for hydrogen scavenging and to describe their main properties with respect to applications. Two main families, Zr and Ti-based materials, are reviewed. Moreover, their ability to efficiently trap hydrogen by suitable preliminary activation process, surface coatings and their resistance to gas impurities is addressed.

Zr-based materials

Non-evaporable getters are frequently made of Zr-based metallic compounds as they chemically sorb active gas molecules, including hydrogen and its isotopes with very good effectiveness. Zirconium can combine with most of the *3d*, *4d* metals and some *p* elements such as C or Al leading to a rich chemistry and allowing to tailor the sorption properties by proper chemical adjustment. Different binary and ternary systems are described and discussed regarding their trapping properties.

Zr-C

These porous getters are obtained from a mixture of pure zirconium and carbon graphite (around Zr 90 wt.%, C 10 wt.%), sintered at high temperature under vacuum. Such treatment leads to high porosity making these materials very efficient for gas sorption. However, they need to be heated at rather high temperature (850 °C) to be activated. Efforts have been made to lower this activation temperature by adding the intermetallic compound LaNi₅ to the Zr and C mixture [25]. Sorption properties at room temperature (RT), as concern both the absorption speed as a function of time and quantity of hydrogen absorbed, have been compared to the non-modified getter (without LaNi₅ addition). Indeed, the modified samples show better absorption properties after activation at lower temperature (700 °C). This improvement is attributed to the formation of catalytic nickel at the getter surface, reducing the activation energy for hydrogen dissociation and thus enhancing the chemisorption into zirconium, following the two steps of surface gas adsorption and bulk diffusion.

Zr-Al

ZrAl alloy (Zr-16Al) can be obtained from calcium hydride production techniques, leading to highly dispersed powders with high specific surface area [26]. Though multiphase, the alloy contains a mixture of binary metallic phases (Zr₃Al₂, Zr₅Al₃, and Zr₄Al₃) able to react and trap hydrogen. Indeed, such highly dispersed materials exhibit hydrogen sorption properties comparable to those of bulk materials with even better results for carbon monoxide sorption.

The sorption properties of the same kind of materials 84Zr–16Al (wt.%) was tentatively modelled by Liu *et al.* [27] with a peculiar focus on the kinetical mechanism. They separate

the mechanism in three steps, i) molecular dissociated chemisorption at the surface, ii) atomic penetration from the surface to the bulk, and bulk diffusion. They were able to solve the rate equations of the three steps simultaneously and they concluded that each process interacts with the other and that both surface effect and diffusion control the absorption rate. Thus, all three steps should be combined to obtain a correct description of the sorption kinetics.

Zr-Co

ZrCo has been widely studied as a NEG, especially for the tritium capture in nuclear applications [21,28]. The hydrogen storage properties of this intermetallic were investigated recently by Jat *et al.* [29]. This cubic alloy absorbs 3 hydrogen atoms per formula unit (H/f.u.) to form an orthorhombic hydride through a two-phase reaction with good kinetics, following a nucleation and growth process. Its low H₂ partial pressure equilibrium at RT makes it of interest for gas gettering.

For a better understanding of the outstanding properties of ZrCo, Chattaraj *et al.* [30] studied the adsorption, dissociation and diffusion of hydrogen at the alloy surface by first principles ab initio thermodynamic calculations. They found that the decomposition of dihydrogen on the (110) surface occurs straightforwardly with a low dissociation barrier (0.7 eV). Additionally, they calculated that the stability of atomic hydrogen decreases from the surface toward the bulk and subsurface.

Though pure ZrCo exhibits good properties as a NEG, several studies were devoted to the addition of other elements for enhancing the sorption and optimizing the activation temperature. For that purpose, rare earth (RE) addition was mainly considered. Nanostructured sintered porous materials were prepared by mechanical alloying of Zr, Co and two rare earths, La and Ce [31]. Effects on the activation process were investigated, showing that lower (280-330 °C) temperature range can be achieved for RE-added materials. This was attributed to the easiest oxidation of rare earths, thus protecting Zr and Co and favoring the getter activation process. The solid solution of REs in Zr and Zr-Co compounds, if any, is very limited [32]. A similar approach was developed by Petti *et al.* [33] who studied Zr-Co-rare earth alloys in the form of sputtered films by XPS at various increasing activation temperature (250-450 °C). From the XPS analysis, they found that surface changes occur mainly above

300 °C with Zr reduction and oxygen depletion at the surface. At higher temperature, cobalt segregation appears to be an important factor to enhance hydrogen pumping in combination with Zr. Following the same concept, milling and adding yttrium to Zr-Co materials was studied [34] regarding the benefit for the activation treatment. They observed that Y addition can reduce the activation temperature by 70 °C and the vacuum preserving time was increased. Again, through chemical analysis, it was concluded that oxygen was slightly depleted from the surface, thus offering more reactive metallic species in contact with the gas phase.

According to the remarkable gettering properties of ZrCo but also its ability to release the stored hydrogen by proper heat treatment, this material has been particularly studied recently for tritium capture in inert gas mixtures and its later recovery. Such concept is foreseen in the frame of the ITER Tritium Plant Storage and Delivery System (SDS) to design the tritium extraction system of the European Test Blanket Modules (TBM)[35,36]. Looking at a prototype storage bed, it was demonstrated that ZrCo-based getter can trap tritium from an incoming He stream. However, the bed geometry remains a key parameter. It was established that the getter performances are only guaranteed up to a limited fraction of the total alloy storage (*i.e.*, 27% of the full capacity). Besides, the desorption step can be achieved only at temperature around 400 °C. The system uses two parallel beds, one for absorption and one for desorption. The absorption bed can absorb up to 0.03 m³ of H₂ at a rate of 8.3 10⁻⁸ m³s⁻¹ in 100 h whereas the desorption occurs in only 10 h. However, during repetitive loading and temperature cycling, the hydride ZrCoH₃ shows some trends to disproportionate to form ZrH₂ and ZrCo₂ [37,38]. Such decomposition of the initial alloy is detrimental to the application as ZrH₂ is much more stable than ZrCoH₃, impeding the tritium recovery from the bed at medium temperature. To mitigate ZrCoH₃ disproportionation upon cycling, the stability of the hydride can be reduced by partial replacement of Zr by Hf [39] and Co by Ni [40] or Cu [41].

Zr-Ni

The system Zr-Ni was the first studied in the field of intermetallic forming hydrides [42]. The binary compound ZrNi exhibits a flat plateau in the composition range from one to 2.5 H/f.u., corresponding to the equilibrium between the monohydride ZrNiH and ZrNiH₃. The pressure range being relatively low at RT temperature makes it interesting for hydrogen storage and trapping. Moreover, ZrNi might trap other species like CO, O₂ or water.

One important application of ZrNi-based getters is their use as reversible vacuum pumps operating in gas-gap heat switches that provide variation of thermal conductance between a hydride bed and a compressor system. It works through the reversible hydrogen uptake between ZrNiH and ZrNiH_{2.5} hydrides with the formation of ZrNiH_{2.5} at 20 °C with equilibrium pressure of ~ 0.1 Pa, and its decomposition back to ZrNiH at 220 °C with an equilibrium pressure of ~ 10⁴ Pa [43]. These devices have been used in Joule-Thomson compressors for sorption cryocoolers that equipped the European Space Agency Planck Mission [44].

The composition Zr (60 wt.%)–Ni (40 wt.%) prepared with by calcium-thermic technology, has been studied by Lavrinenko *et al.* [45] to be considered as a NEG for nuclear power plant (NPP). It consists of a mixture of ZrNi and Zr₂Ni compounds. Desorption analysis allows to establish that gas release takes place above 400 °C, attributed to water, then above 450 °C related to hydrogen desorption. The close composition Zr (62 wt.%)–Ni (38 wt.%) has been produced by Aksyonova *et al.* [46], using the same calcio-thermal synthesis and forming again a mixture of ZrNi and Zr₂Ni. The material absorbs hydrogen with an equilibrium pressure of 1 Pa at RT. The hydrogen release was analyzed by temperature programmed desorption (TPD) up to 930 °C. Curve analysis allows to assign the hydrogen bond energy in the material in the range 207–250 kJ/mol.

The same material was also considered for the Japan Materials Testing Reactor (JMTR) as a tritium gas getter [47]. To improve the gettering properties, various transition elements (mainly Co and Fe) were added to the alloy, to form the pseudo-binary ZrNi_{1-x-y}Co_xFe_y. From PCI measurements, it was found that such chemical modifications lead to plateau pressures comparable to that of depleted uranium (*i.e.*, of the order of 4 10⁻⁴ Pa at RT) for ZrNi_{0.2}Co_{0.7}Fe_{0.1} and ZrNi_{0.3}Co_{0.5}Fe_{0.2}. Moreover, such compositions show good behavior in powder form when exposed to air, without noticeable pyrophoricity, making them easy to handle. Post-hydrogenation analysis by X-ray diffraction indicated that for ZrNi_{0.3}Co_{0.5}Fe_{0.2}, some disproportionation reaction occurs with the formation of ZrH₂ and ZrNi-type compounds.

Zr-V

The Zr-V system was investigated by Mantolín *et al.* [48]. Activation process of a $Zr_{44}V_{56}$ layer (500 μm thick) deposited on a stainless-steel substrate was investigated by X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectroscopy (SSIMS). Depending on the activation temperature, ranging from 120 to 320 $^{\circ}\text{C}$, the ion intensity variations of VO^+/V^+ and VH^+/V^+ indicate an increasing depletion of the surface oxide layer to partially reduce oxides and an enhancing of the metal-hydrogen interaction. It was also found that the vanadium oxide reduction was faster than the Zr one, favoring first V hydrogenation, followed by Zr. However, such effects are found significant only for temperature above 200 $^{\circ}\text{C}$.

Zr-Fe

The intermetallic compound Zr_2Fe has been foreseen as a suitable non-evaporable getter as it can react with hydrogen (and its isotopes), oxygen and water but remains inactive toward nitrogen and has good stability in air. This compound exists in a narrow range of composition and temperature in the phase diagram [49]. It does form a hydride $ZrFe_2H_{4.5}$ at low temperature (-23 $^{\circ}\text{C}$) [50] but decomposes into ZrH_2 and $ZrFe_2$ at higher temperature (typically 500 $^{\circ}\text{C}$).

As most of the NEG's, Zr_2Fe needs to be thermally activated before used as a scavenger. Nobile *et al.* [23] studied the behavior of such alloy depending on the temperature, time and vacuum pressure for the activation process. They used a commercial alloy (SAES St 198) made of Zr_2Fe as the main phase but also containing some secondary phases like $ZrFe_2$, Zr_5FeSn , α -Zr and Zr_6Fe_3O . They found that the absorption rate of deuterium was faster if the material was activated at 350 $^{\circ}\text{C}$ under a vacuum of at least $3 \cdot 10^{-4}$ Pa or at 500 $^{\circ}\text{C}$ whatever the vacuum value, compared to activation at only 350 $^{\circ}\text{C}$ and poor vacuum (2.5 Pa). The deuterium content of the Zr_2Fe phase is reported to be below 3 D/f.u.. They also determined the Pressure-Composition-Isotherm (PCI) curves in the range 200 to 500 $^{\circ}\text{C}$. They observed that the PCI absorption isotherm can be described by only one reaction for temperature below 350 $^{\circ}\text{C}$ while above this temperature, the sorption mechanism takes place following at least two steps. From X-ray diffraction, they concluded that the deuteride decomposes first into ZrD_2 and $ZrFe_2$, then into ZrD_2 and pure Fe. Though this decomposition does not affect the trapping

properties of the material, it hinders the possible recovery of the stored hydrogen isotopes as hydrogenated zirconium is too stable. Indeed, such disproportionation reaction can easily take place by hydrogen sorption at high temperature and might limit the application of the Zr_2Fe alloy for isotope recovery. Song *et al.* [51] studied this disproportionation reaction and defined some optimal conditions for the activation process that should be limited to 400 °C for 3h. They also determined that absorption should be better managed at 300 °C and 0.1 MPa of gas pressure, reaching then a capacity of 1.53 wt.%.

Though resistant to corrosion, Zr_2Fe might be oxidized, especially during the activation process, to form a passivation layer that would slow down the kinetics of the sorption reaction. Cohen *et al.* [52] investigated the oxidation process, using a crushed St-198® material in the temperature range 320-500 °C with a argon gas flow containing various oxygen contents (0.1%, 0.7%, and 8%). From X-ray and calorimetric measurements, they established that the oxidation process induces first the formation of zirconium oxide (ZrO_2) and pure iron (Fe), followed by the full oxidation of the material, forming Fe_2O_3 . From kinetic analysis, they also found that below 320 °C, a near-passivating oxide layer is formed at the surface whereas at higher temperature, the reaction is controlled by mass transfer. Thus, above 320 °C, oxygen impurities react in the outer shell of the material while the material bulk remains active for hydrogen trapping.

Beside bulk or powder materials, Zr_2Fe was also studied in the form of melt spun ribbons [53], the objective being to introduce a H_2 trap in the outer shell of high pressure storage reservoirs (70 MPa) to mitigate small leaks. 25 μm thick ribbons were obtained, containing a mixture of cubic metastable Zr_2Fe and an amorphous phase. Annealing at 500 °C recrystallizes the amorphous phase into cubic Zr_2Fe , or more probably its oxidized form $\eta-Zr_4Fe_2O_x$, as this phase is known to be stabilized by small amount of oxygen [54]. It is worth noting that formation of stable oxygen-containing intermetallic η -phases is a feature of not only Zr-Fe-(O) system but also many other systems comprising Zr (and/or Ti) together with other transition metals (*e.g.*, V) and non-metal Z = O, B, N; to form, for example, $Zr_3V_3Z_x$ [55–57]. The as-spun ribbons show very slow absorption rate at RT (full hydrogenation in 6 h) whereas annealed ribbons absorb readily hydrogen in 30 s though a reduced capacity by 33%, attributed to an

absorption–disproportionation reaction. Nevertheless, such ribbons exhibit very good sorption properties, even in oxidized atmosphere.

Zr-(Ti)-V-Fe

Beside binary systems, few ternary systems have been considered as material for hydrogen gettering. Fe-poor Zr-V-Fe alloys (*i.e.*, Fe < 11.1 at.%) were proposed by SAES Getters. For instance, they produced the trade name St-172[®], a material investigated by [58] obtained from an equal mixture of pure Zr and St-707[®] with nominal weight composition 70.0Zr-24.6V-5.4Fe (wt.%). Combined structural (XRD) and chemical (EDX) analysis shows that the compound contains a mixture of α -Zr (with V \sim 1 at.%, and Fe \sim 0.6 at.%), and the cubic MgCu₂-type phase Zr(V_{0.84}Fe_{0.16})₂. Besides, about 30 % of Zr₃(V_{0.84}Fe_{0.16})₃O_x, and 1~2% of zirconium oxide and hydride are also reported. PCI curves were measured between 100 and 400 °C and heating cooling cycles were performed. The authors observed some hydrogen release up to 427 °C, attributed to some reversibility of Zr(V_{0.84}Fe_{0.16})₂ and Zr₃(V_{0.84}Fe_{0.16})₃O_x but a large part of the hydrogen remains trapped in the highly stable α -Zr phase, at least in this temperature range. The similar composition Zr₇₀V_{24,6}Fe_{5,4} was studied during hydrogen cycling by Roupcová and Schneeweiss [59]. The latter authors observed from both X-ray diffraction and Mössbauer spectroscopy that the hydrogen-free sample contains a cubic Laves phase and α -Zr whereas the loaded material is made of the two hydrides ZrV₂H_{3,6} and ZrH₂. They also observed that upon cycling, the amount of zirconium oxides increased and some amorphization occurred, inducing a loss of the overall sorption properties.

Park *et al.* [60] studied a composition slightly richer in vanadium Zr₅₇V₃₆Fe₇. They observed two phases, mainly cubic Zr(Fe,V)₂ coexisting with α -Zr. Investigations of the activation process and sorption properties lead to the conclusion that α -Zr is more easily activated in the presence of the Laves phase, probably due to some better oxide reduction for this latter phase. Once activated, zirconium fully participates to the sorption reaction. The same composition was analyzed by Feng *et al.* [61], regarding the sorption properties at low temperatures (around -170 °C). Though exhibiting slow kinetics, the sample shows good hydrogen capacity retention at low temperature.

Leng *et al.* [62] varied the zirconium amount in the composition Zr_xV_5Fe (with $x_{Zr} = 3, 5, 7, 8, 9$) to check the role of Zr addition on the gettering properties. For all x_{Zr} values, they found the coexistence of α -Zr and cubic $Zr(Fe,V)_2$, with weight ratio varying from 25 to 48 wt.% of α -Zr depending on x . From PCI curves, low pressure plateaus are observed for all compounds, but $x_{Zr} = 3$. The plateau width increases with x_{Zr} and its equilibrium pressure decreases. The second slopy branch of the PCI is attributed to the hydrogenation of $Zr(Fe,V)_2$. The best sorption properties are obtained for Zr_7V_5Fe , both from the thermodynamic and kinetic points of view. This is attributed to the small size of the particles and a better phase distribution between the two components.

A close composition $Zr_xTi_{7-x}V_5Fe$ ($x_{Zr} = 0, 0.3, 0.9, 1.5$ and 2.1) was also considered by Han *et al.* [63], but adding some titanium on the Zr side. Again, two phases are observed, α -Zr type and the cubic C15 Laves. Increasing x up to 1.5 induces a decrease of the α -Zr amount whereas the cubic one behaves the opposite. Cell volumes follow approximately the same variations (decreasing volume for α -Zr and increasing one for C15 up to $x_{Zr} = 1.5$). Those effects are related to variation of the composition in both phases. Regarding H sorption, again a low-pressure plateau-like branch was attributed to zirconium, followed by a sloping branch assigned to the Laves phase. Ti substitution for Zr lowered the sorption pressure of the C15 and increased the amount of α -Zr. It is also reported that, though the H-content increases with x_{Zr} , Ti addition leads to larger size of the particles upon cycling, thus reducing the sorption kinetics.

Ti-based materials

Either as an alternative to Zr-based metallic compounds, or to tune their physicochemical and functional properties, Ti-based materials have also been widely proposed as NEG. Owing to the close chemical properties of Ti and Zr as group 4 elements, they are fully miscible and form analogous hydride compounds, being those of titanium slightly less stable than those of zirconium.

Ti-Mo

Ti-Mo getters have been studied by Giorgi *et al.* in the 90's [64]. Besides aiming at achieving high sorption efficiency, Ti-Mo getters are expected to have good mechanical strength. They were produced in the form of porous disks after sintering Ti-10wt.%Mo powder mixtures in the range 800-1000 °C. The total porosity was ~ 40% with an average pore diameter of 4 μm. The getters could be activated by thermal heating above 500 °C allowing pumping speeds of the order of $10^{-3} \text{ m}^3\text{s}^{-1}$ at room temperature. Equilibrium hydrogen pressures concur with those of the Ti-H system which was assigned to the negligible solubility of hydrogen in Mo.

The Ti-Mo system has been later studied by Zhou *et al.* for Mo-contents ranging from 0 to 12.5 wt.% [65]. Elemental powders were mixed by ball milling, pelletized at 400 MPa and sintered at 900 °C. XRD analysis shows the formation of *hcp*-Ti, *bcc*-Mo and *bcc*-β(Ti,Mo) solid solution. The porosity of the pellets as a function of Mo-content reaches a maximum of 38 % at 7.5 wt.%, for which the fastest hydrogen sorption speed is observed. In a subsequent work [66], the same research group demonstrated that Ti-7.5wt.% Mo getter can be gradually activated on increasing the activation temperature from 500 to 750 °C. After activation treatment at 750 °C, the getter absorbs hydrogen at a pumping speed of $0.007 \text{ m}^3\text{s}^{-1}\text{g}^{-1}$ at room temperature, increasing up to almost $0.02 \text{ m}^3\text{s}^{-1}\text{g}^{-1}$ at 400 °C. This work demonstrates the major role of porosity on the sorption properties of Ti-Mo alloys, a parameter that can be tuned using advanced elaboration methods such as metal injection molding [67].

Ti-Co-Ce

Ti-Co-Ce alloys have been recently proposed as bulk getters for MEMS applications [32]. Their chemistry and properties are closely related to the previously reviewed Zr-Co family with the addition of rare earths. Two Ti-Co-Ce alloys with chemical composition (wt.%) 71Ti-24Co-5Ce and 80Ti-15Co-5Ce were elaborated by arc-melting and their properties compared to 81Zr-14Co-5Ce (St 787® from SAES). Both Ti-based getters consist of *hcp*-Ti phase, cubic Ti₂Co and Ce oxide. Ce has negligible solution in Ti-containing phases. Those Ti-based getters have higher hydrogen sorption capacity and faster sorption properties than the Zr-one and the performances improve with Ti-content. Fast sorption was assigned to enhanced hydrogen diffusion through Ti/Ti₂Co interfaces. Ti-Co-Ce alloys were activated at 350 °C for 30 min.

Ti-Zr-V

In the beginning of this century, Ti-Zr-V NEG films have been extensively studied at CERN for being used in particle accelerators [68–70]. The getters were synthesized as $\sim 1 \mu\text{m}$ thick films deposited over stainless-steel substrates using a three-cathode DC magnetron sputtering system and three individual metal targets [70]. To map suitable alloy compositions, their activation ability was foreseen by Auger Electron Spectroscopy (AES) by evaluating the parameter R defined as the ratio between the intensity of metallic Zr peak at 147 eV and the peak at 141 eV characteristic of Zr in ZrO_2 after annealing of the films at 200°C . The concept behind this approach is that activation of NEG getters towards hydrogen trapping requires as a prerequisite the reduction of native transition metal oxides. Thus, it was established that alloys with criterion $R > 0.5$ (empty symbols in Figure 2a) are expected to efficiently trap hydrogen. Thus, from AES analysis, close to equiatomic Ti-V-Zr and Ti-poor V-Zr compositions were identified as promising getters. Additionally, structural measurements by XRD revealed that alloy compositions with $R > 0.5$ have low crystallinity with crystal sizes below 5 nm (empty symbols and stars in Figure 2b). After annealing at 200°C , the clear correlation displayed in Figure 2 between surface composition and bulk crystallinity was assigned to the fact that the nanocrystalline structure enhances oxygen solubility and diffusivity in the bulk during the activation treatment.

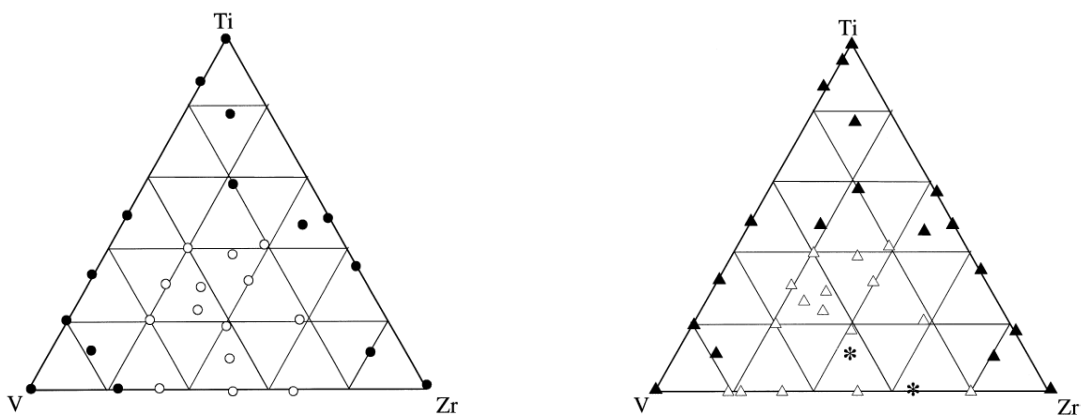


Figure 2 - a) Categorization of Ti-Zr-V alloys as a function of the R criterion: empty and full symbols for R higher and lower than 0.5, respectively. Reprinted with permission from [70]. b) Categorization of Ti-Zr-V alloys as a function of grain size: full triangles represent films with grains larger than 100 nm, empty triangles stand for nanocrystalline films (grain size of 3-5 nm), and stars represent amorphous films Reprinted with permission from [70]. Copyright 2001, Elsevier.

Benvenuti *et al.* [68] confirmed that Ti-Zr-V alloys fulfilling the quality criterion ($R > 0.5$) are good hydrogen getters after annealing treatment at 180 °C for 24 h, enabling to reach ultimate vacuum pressures down to 10^{-11} Pa. The measured sticking factors (*i.e.* the number of adsorbate molecules that stick to the getter surface compared to the total number of molecules that impinge on it during the same period of time) ranged between $6 \cdot 10^{-3}$ and $5 \cdot 10^{-2}$ for H_2 and between 0.4 and 0.8 for CO. These sticking factors as well the CO saturation capacity are rather low as result of the smooth surface of the films. Complementary surface experiments by Electron-Stimulated Desorption (ESD) have demonstrated that hydrogen is incorporated into the bulk while carbon monoxide stays chemisorbed on the getter surface [71].

In an accompanying publication, the group of Benvenuti *et al.* studied in detail the gettering properties of $Ti_{32}Zr_{16}V_{52}$ film, 1.2 μm in thickness, and deposited over copper or stainless-steel substrates [69]. During the activation process, AES analysis revealed that the surface oxide is progressively reduced above 160 °C with increasing formation of metallic surface. This process is independent of the substrate composition. The functional properties were determined for different gases CO, N_2 and H_2 by pumping speed measurements, which are directly linked to sticking probabilities. A noticeable sticking probability for H_2 was detected above 180 °C which increases up to 1% between 230 and 250 °C. Interestingly, it was noticed that the pumping speed of hydrogen diminishes by a factor of 2 if the film was previously exposed to a small amount of CO (1×10^{14} molecules cm^{-2}) due to their smooth surface.

Valizadeh *et al.* [72] have compared the activation temperatures of Ti-Zr-V thin films prepared from targets made up of either three elemental twisted wires or equiatomic Ti-Zr-V alloy. The authors demonstrated that the use of an alloy target produces getter films with high chemical homogeneity. Its composition is $Ti_{34}Zr_{29}V_{37}$ with chemical fluctuations below the statistical accuracy of EDX (2 at.%). The getter crystallizes in *bcc* β -Ti structure with grain-size between 5 and 6 nm. The film has a columnar microstructure, which is argued to favour diffusion of oxygen in the bulk through grain boundaries during the activation process. Consequently, the activation temperature was reduced to 160 °C, *i.e.*, 20 °C less than for films produced from targets using three twisted wires.

Very recently, Wang *et al.* [73] have performed chemical surface analysis of a Ti-Zr-V alloy by *in-situ* synchrotron radiation XPS. Experiments were conducted during activation for 1 h within the temperature range 150-180 °C in ultra-high vacuum ($1.5 \cdot 10^{-5}$ Pa). The film composition was determined as $Ti_{29.5}Zr_{33.2}V_{29.8}O_{7.5}$ by Energy Dispersive Spectroscopy (EDX). Oxides TiO_2 , ZrO_2 and V_2O_5 were detected by XPS as main surface components. The alloy had a significant porosity (5%) and surface roughness ($R_{average} = 59$ nm). The activation of the films starts at 150 °C through the reduction of oxides following the order V_2O_5 , TiO_2 and ZrO_2 . These results concur with secondary ion mass spectroscopy analysis proving the enhanced performance of Ti-Zr-V alloys compared to the individual metals [74]. The microstructure of the films could be modified using different sputtering parameters [75].

Ti-Zr-Hf-V

Malyshev *et al.* reported for the first time that quaternary Ti-Zr-Hf-V alloys have superior gettering properties – *e.g.* activation temperature, H_2 and CO sticking probabilities and CO pumping capacity- than the previously reviewed Ti-Zr-V system [76]. For the almost stoichiometric getter, $Ti_{27}Zr_{25}Hf_{27}V_{21}$, which can be classified as a *bcc*-type high entropy alloy [77], the lowest activation temperature was obtained in the range of 140-150 °C. The getter was obtained as 1 μm thick film with columnar microstructure and grain size between 2 and 4 nm. The getter film was deposited from an alloy target using a solenoidal magnetron facility working in DC mode. Similarly as for the ternary alloy [72], the alloy target provides lower activation temperature than twisted elemental wires.

The film microstructure plays a major role on the gettering properties of Ti-Zr-Hf-V alloys [78,79]. The columnar structure provides a higher pumping property to absorb hydrogen from the vacuum line but, as a drawback, offers fast channels for the hydrogen diffusion of atoms dissolved in the stainless-steel substrate through the NEG layer [79]. To solve this issue, Malyshev *et al.* [78] have deposited a dual-layer nonevaporable getter where a 0.5 μm thick dense layer was deposited first on stainless-steel substrate and a 1 μm thick columnar layer was then deposited on the top (Figure 3). Columnar and dense thin film microstructures were obtained using DC and pulsed DC modes, respectively. This dual-layer combined the advantages of limited Electron-Stimulated Desorption (ESD) of hydrogen for the dense layer and good pumping properties of the columnar layer. The most suitable activation temperature

varied between 150 and 180 °C for which sticking probabilities for H₂ and CO gases showed significant variations as a function of ESD doses.

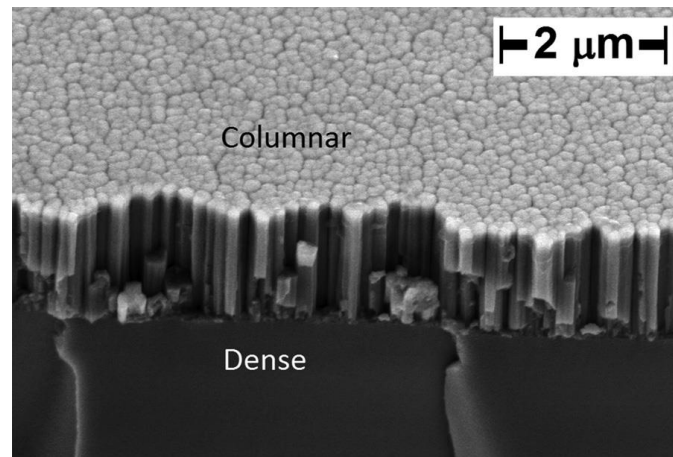


Figure 3 - Cross-section SEM micrograph of a dual-layer film $Ti_{25}Zr_{25}Hf_{25}V_{25}$ showing a dense alloy layer covered by a 1 μm columnar structure. Reprinted with permission from [78]. Copyright 2016, American Vacuum Society.

Recently, Ge *et al.* [80] have carried out an *in situ* synchrotron XPS comparative study on quaternary and Hf-free ternary getters elaborated by DC magnetron sputtering with a cathode target formed by twisted metal wires. The grain size of the quaternary target is reported to be smaller than that of a ternary Ti-Zr-V target under same preparation conditions. By analyzing the full XPS spectra and in particular XPS peaks assigned to Hf, Zr, Ti, V, C and O signals at different temperatures, it was observed that the oxides of Ti and V are reduced to the metal state at 150 °C, whereas those of Hf and Zr are reduced to 130 °C. It was then confirmed that the addition of Hf is crucial to reduce the activation temperature in this target Ti-Zr-Hf-V family.

Surface coating

In addition to the intrinsic properties of hydrogen absorbing alloys, which define the H content and the trapping pressure at a given temperature, the surface chemistry plays a crucial role in the sorption kinetics. Most of the metallic elements composing the alloys are indeed very reactive and easily form oxides (or hydroxides) at the surface. Thus, to trigger the first absorption, high temperature activation processes are commonly reported for these materials. Such a thermal treatment aims to remove the hydrogen barrier species on the surface by reduction or dilution. Although effective in activating the material, this treatment is not compatible for certain applications (*e.g.* in particle accelerators [73]) and does not

prevent the rapid reformation of surface passivation species. Another approach consists in coating the surface of the gettering material with a thin layer of a weakly oxidizing compound, protecting the surface but allowing hydrogen permeation toward the scavenger.

To achieve such protecting layer, platinum group metals (PGM) are undoubtedly the best choice as they are highly resistant to corrosion. In addition, among the seven PGM, Palladium is of peculiar interest as it forms a hydride $\text{PdH}_{0.7}$ near ambient conditions ($P_{\text{eq}} \approx 0.67 \cdot 10^5$ Pa at RT). Thus, thanks to its molecular hydrogen dissociation properties, Pd can play a very beneficial catalytic role on the surface.

Pd-coating

Such approach has been mainly developed for Zr-based alloys. Using radio frequency magnetron sputtering, Zhang *et al.* [81] deposited a thin film of palladium on various Laves phases (ZrV_2 and $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{V}_2$). They found that the Pd layer was oriented along the preferred crystallographic axis (111) of the *fcc* structure. Though the coating did not hinder the absorption capacity of the getters, it leads to a significant decrease of the sorption rate by about 40%. The authors attribute this phenomenon to the difference between the diffusion rates of hydrogen in Pd and Zr alloys and interface resistance. Pd coating of ZrNi in powder form was also attempted by Ashida *et al.* [82] using electroless plating. A subsequent thermal treatment at 800 °C leads to the formation of ZrPd at the material surface. The coating did not change the sorption properties of ZrNi but protects it compared to the bare material that loses its sorption properties due to surface re-oxidation. This was attributed to the better resistance to corrosion of ZrPd by comparison to ZrNi.

Palladium coating has been also widely developed for protecting Ti-Zr-V getters. Such materials can be produced as thin films by magnetron sputtering that can be finely covered by a layer of Pd [83] as shown in Figure 4.

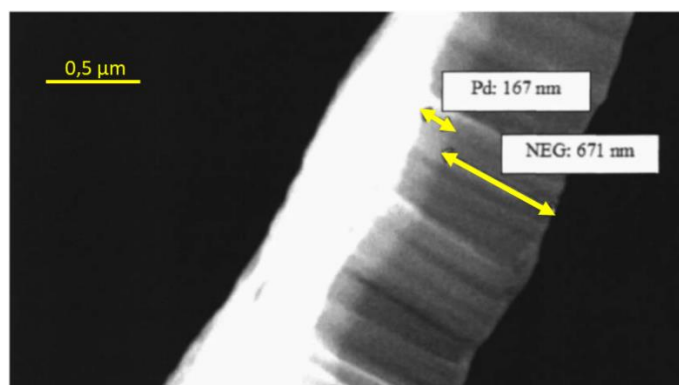


Figure 4 - Scanning electron microscopy (SEM) image showing a TiZrV film coated by a Pd overlayer. The arrows indicate typical thickness. Reprinted with permission from [83]. Copyright 2008, American Vacuum Society.

Such combination of a gettering alloy and palladium coating leads to improved kinetics of one order of magnitude regarding hydrogen trapping. The same coating technique was proposed by Mi *et al.* [84] to sputter Pd on the surface of $Zr_{70}Fe_{5.4}V_{24.6}$ (St-707[®]). They observed that *fcc* Pd was preferentially oriented along (111), as reported by Zhang *et al.* [81]. However, they did not observe peculiar effects, neither for the kinetics nor for the activation process. They noticed better sorption properties with an increase of the capacity, the enthalpy, and the entropy of hydrogenation leading to the conclusion that a more stable hydride was formed. With the same approach, Zhang *et al.* [85] used electroless plating technique to cover $Zr_{70}Fe_{5.4}V_{24.6}$ with palladium. They confirm the uniform deposition of metallic Pd on the alloy surface and compared the absorption rates of the bare and covered materials with pure and 1 vol.% air-contaminated hydrogen. They observed significant improvement in the sorption rate for the Pd-coated material in pure hydrogen but also for the contaminated one, without losing capacity. From XPS analysis, they attributed this better behavior to the reduction by 12% of the Zr oxide at the surface for the Pd-coated getter.

Beside Ti-Zr-V, surface coating of a ZrCo-type ($Zr_{76.2}Co_{20.7}Ce_{3.1}$) thin film was also proposed by [86] using DC magnetron sputtering. The film thickness was 2.3 μm topped by 400 nm of palladium. They found that the Pd coating was efficient to protect the getter from oxidation, as metallic Zr was still observed at the surface when exposed to air, contrary to the bare sample for which zirconium oxide is likely formed. This led to significant improvement of the sorption properties, retarding initial rate and capacity.

Pure titanium can be also used as an efficient NEG pump if its surface, which is naturally covered by passivating oxides, can be protected against oxidation by depositing a Pd coating.

Miyazawa *et al.* [87] recently studied the trapping properties of 1.3 μm Ti film coated with 50 nm Pd overlayer. The double-layer film was deposited by consecutive sublimation of Ti and Pd filaments under UHV conditions (base pressure of $1.8 \cdot 10^{-8}$ Pa) to minimize oxygen content in the Ti layer. Oxygen content was evaluated by XPS to be less than 0.05%. The film could be activated at baking temperatures as low as 133 $^{\circ}\text{C}$ for 12 h time and, more efficiently, at 176 $^{\circ}\text{C}$ for 3.5 h. Under these conditions, the equilibrium pressure in closed volume reached $4.6 \cdot 10^{-6}$ and $1.7 \cdot 10^{-7}$ Pa with pumping speeds of $2.8 \cdot 10^{-5}$ and $2.3 \cdot 10^{-5} \text{ m}^3\text{s}^{-1}$, respectively. Complementary studies by the same group [88] show that hydrogen sorption rates are preserved during several hydrogen absorption/desorption cycles for temperature swings between 20 and 240 $^{\circ}\text{C}$. However, activation temperatures above 280 $^{\circ}\text{C}$ induce segregation of Ti to the Pd surface promoting the formation of titanium oxides. The ability of Ti/Pd films to absorb hydrogen is completely lost by annealing at 500 $^{\circ}\text{C}$. A step forward has been proposed by Lim *et al.* [89] with the preparation of nano-engineered multilayer composite films, combining titanium nanoparticles covered by a palladium layer. Such 600 nm-thick Ti20%-Pd film topped with a 35 nm-thick Pd was deposited on a Si wafer by co-sputtering and post-vacuum-annealing. Heat treatment leads first to the segregation of titanium atoms that aggregate separately from Pd. Reaching an annealing temperature of 400 $^{\circ}\text{C}$, a dewetting of the Pd film coverage is obtained, allowing the nanosized Ti aggregates to trap hydrogen.

Pd-Ag coating

Though pure palladium is mostly used as a coating element, some palladium alloys have also been considered with the aim of circumventing the brittleness of pure Pd-coating, associated to mechanical stress during Pd/PdH $_{\sim 0.7}$ phase transition, and enhancing the H permeability by beneficial alloying effects. This is the case with Pd-Ag coating that has been used to cover by electroless plating various zirconium-based getters such as the Laves phases ZrV $_2$ and Zr $_{0.9}$ Ti $_{0.1}$ V $_2$ or Zr $_{57}$ V $_{36}$ Fe $_7$ (at.%) [90]. This coating covers the surface homogeneously, improving both activation and kinetics but slightly decreasing the sorption capacity, especially for hydrogen gas containing 1 vol.% air. Indeed, the Pd-Ag coating preserves the alloy surface from poisoning and maintains a good linkage with the surface after six sorption cycles.

Ni coating

Unlike protective layers based on PGM metals, sacrificial layers such as Ni have been also proposed to circumvent the issues of Ti-getters due to their passivation by native oxides [19]. The idea, though not supported by thermodynamic data on oxide stability, is that the sacrificial layer can pick-up oxygen from TiO₂ during the activation treatment and pure titanium forms at the getter surface. Alternatively, it can be suggested that TiO₂ would react with Ni to form Ti-Ni-O compounds able to chemisorb hydrogen. Following this sacrificial layer approach, 1 μm Ti films covered with 30 nm of Ni were activated at temperatures of the order of 300 °C [19].

Resistance to impurities

The development of efficient hydrogen NEG's must be considered in relation to their applications. Most of the time, the objective is to separate and trap hydrogen gas (or its isotopes) diluted in a mixture of other species. Consequently, the resistance to impurities of these gettering materials is a key parameter to assess. Various gases have been considered so far (N₂, O₂, CO₂, CO, CH₄, NH₃...), the former naturally existing in air, the latter frequently formed during hydrogen production or handling.

Nitrogen

N₂ is commonly found in gas mixture as it represents 78%vol. in air composition. Several gettering materials have been tested with nitrogen gas mixed with dihydrogen. The commercial getter from SAES St-198®, a Zr-Fe based alloy still absorbs hydrogen at temperatures up to 425 °C without noticeable limitation [91]. However, Abboud and Montanabbir [92] report the possible formation of ZrN for Zr-Co-RE when activated at 350 °C, this surface layer being detrimental for hydrogen sorption at room temperature. Similar effects are described by Zhang *et al.* [93] for an annealed Zr_{0.9}Ti_{0.1}V₂ alloy exposed to N₂ for several minutes (0.5 to 3 min) at room temperature. The sorption properties are limited after such exposure due to surface poisoning but can be however regenerated by degassing the materials in vacuum at 550 °C for 10 min.

The use as nitrogen getters of multi-layered thin films with controlled microstructure for MEMS applications have been proposed by Bourim *et al.* [94]. Ti and Ti-Zr bilayers were deposited over Si-substrates with or without Ru seed interface. The Ru seed promotes the formation of columnar microstructure with high surface roughness for Ti and Zr getters and thereby reduces activation temperatures by at least 25 °C. Potentially, the getters could be activated at 250 °C but in practice, due to the formation of blocking surface carbides, activation temperature of 375 °C is required. Protective coatings such as PGMs are suggested to be employed to prevent carbon poisoning.

Oxygen

O₂ poisoning has been particularly studied, as metallic hydride getters are usually very sensitive to oxidation. In presence of oxygen, most authors report the formation of an oxide (or hydroxide) layer inhibiting the hydrogen sorption [91–93]. The layer thickness is found to be dependent of the activation temperature and can reach several tens of nanometers. Activation process allows to partly reduce the oxides though preventing the formation of such barrier should be anticipated by proper optimization of the composition.

Carbone dioxide

Carbone dioxide (CO₂) was found to be dissociated into CO and O⁻ at the surface of a Zr-Co-RE alloy [92]. The carbon monoxide remains adsorbed at the surface whereas the O⁻ species are susceptible to diffuse deeper in the material, possibly forming oxides.

Carbone monoxide

Carbone monoxide (CO) is known to be detrimental for hydrogen absorption as it blocks the active sorption sites at the metal surface. Indeed, James and Morgan [91] observe that for the activated St-198[®] getter, deactivation at room temperature appears at the earlier stage (becoming total after 12 h) in the CO-containing gas mixture (0.1 vol.% H₂/ 0.1 vol.% CO / 99.8 vol.% N₂). However, they also report that this sorption diminution is less important at 350 °C though the gettering efficiency is still reduced by 33% compared to the CO-free mixture. Similar behavior was reported for ZrCo, Zr₂Fe and Zr-rich Zr-Ti-V alloys. After activation, they were tested toward hydrogen sorption using 5 vol.% CO / 95 vol.% H₂ at room

temperature. They observed that the presence of CO in the mixture noticeably decelerates the sorption rate of the alloys but indicate that they still display noteworthy gettering properties. However, the time scale is significantly extended by several orders of magnitude.

Methane

Beside other gases, CH₄ was also considered as it can contaminate hydrogen when produced by natural gas reforming. James and Morgan [91] report on the sorption properties of St-198[®] with the mixture (0.1 vol.% H₂/ 0.1 vol.% CH₄ / 99.8 vol.% N₂). At 350 °C, the gettering properties are almost not affected. At room temperature, the gettering properties are reduced by 33%, a value comparable to that observed for CO.

Ammonia

NH₃ is reported to dramatically slow down the gettering properties of St-198[®] at a level of 4 vol.% and 350 °C by a factor of ten [95]. James and Morgan [91] confirmed these observations, losing the gettering properties of the same material at ambient temperature and lower concentrations (0.13-0.10 vol.% H₂/ 0.10-0.05 vol.% NH₃ / remainder vol.% N₂). They concluded that the deactivation is highly dependent on the temperature and slightly on the NH₃ concentration.

Discussions and Conclusions

Most of the hydrogen-trapping alloys are made of a hydride-forming elements from group 4, either Ti or Zr, two atoms forming very stable hydrides at room temperature ($\Delta H^\circ \sim -140$ to -170 kJ/mol.H₂). Representative getter families surveyed in this review with their main hydrogenation characteristics are gathered in Table 1. Zirconium is generally alloyed with other 3d transition metals (V, Fe, Co, Ni) with lower affinity for hydrogen or with *p* elements like carbon or aluminum. Besides, titanium-based getters also exhibit a complex chemistry by forming some ternary alloys involving 4d transition metals (Mo, Co, Hf) and occasionally in combination with zirconium. In all cases, such compositions aim at fulfilling the gettering conditions for very low equilibrium pressure, high hydrogen saturation capacity, fast sorption kinetic, and high resistance to gas impurities.

Table 1: Composition, morphology, and hydrogenation properties of representative getter materials. For the measurement method, A, B and C stand for pressure variation, dynamic, and Sieverts' methods, respectively

Family	Composition	Form	Powder size or film thickness (μm)	Activation		Equilibrium		Sorption Capacity				Absorption rate			Method	Ref.	
				T(°C)	t(min)	P(Pa)	T(°C)	Value	Units	T(°C)	P(Pa)	Value	Units	T(°C)			
84Zr-16Al	typically: Zr ₃ Al ₂ , Zr ₅ Al ₃ , Zr ₄ Al ₃ (90Zr + 10C) + 10LaNi ₅	Ribbon		750	30			1.7 10 ⁻⁴	Pa m ³	70			9 10 ⁻³	m ³ s ⁻¹	70	A	[27]
Zr-C+LaNi ₅	(90Zr + 10C) + 10LaNi ₅	Pellets	63.5	700	30			12.2	Pa m ³ m ²	20			3.78 10 ⁻³	Pa.m ³ s ⁻¹ m ²	20	B	[25]
Zr-C+LaNi ₅	(90Zr + 10C) + 10LaNi ₅	Pellets	63.5	850	10			14	Pa m ³ m ²	20			5.27 10 ⁻³	Pa.m ³ s ⁻¹ m ²	20	B	[25]
Zr-C	90Zr + 10C	Pellets	63.5	850	10			7.8	Pa m ³ m ²	20			2.67 10 ⁻³	Pa.m ³ s ⁻¹ m ²	20	B	[25]
Zr ₂ Fe	crystalline-Zr ₂ FeO _x	Ribbon	25	500				1.2	wt.%	25	1 10 ⁶		0.04	wt.% s ⁻¹	25	C	[53]
Zr ₂ Fe	crystalline + amorphous-Zr ₂ FeO _x	Ribbon	25	20	none			1.8	wt.%	25	1 10 ⁶		1.4 10 ⁻⁴	wt.% s ⁻¹	25	C	[53]
Zr ₂ Fe (St-198)	Zr ₂ Fe + (ZrFe ₂ , Zr ₃ FeSn, α-Zr, Zr ₆ Fe ₃ O)	Pellets	150	350-500	240-960			14-10	Pa m ³ g ⁻¹	200-500	1 10 ³		0.414	Pa.m ³ s ⁻¹ g ⁻¹		C	[23]
Zr ₂ Fe	Zr ₂ Fe + Zr ₂ FeO _x	Powder	75-150	300-500	180			1.76-1.85	wt.%	25	1 10 ⁵		0.05	wt.% s ⁻¹	25	C	[51]
75Zr-22Co + (1.5La, 1.5Ce)	Zr ₃ Co+ZrO ₂ +Co ₂ O ₃	Pellets	1	330	60											A	[31]
75Zr-22Co + (3Y)	Zr ₃ Co+ZrO ₂ +Co ₂ O ₃	Pellets	0.05	360	80	2 10 ⁻⁴										A	[34]
ZrNi(Fe,Co)	ZrNi _{0.3} Co _{0.5} Fe _{0.2} α-Zr + C15	Powder	300	500	840	4 10 ⁻⁴	20	0.54	wt.%	20	1 10 ⁵					C	[47]
70Zr-24.6V-5.5Fe (St-172)	Zr(V _{0.84} Fe _{0.16}) ₂ + Zr ₃ (V _{0.84} Fe _{0.16}) ₃ O _x + ZrO _x + ZrH ₂	Pellets	100	400		1 10 ³	400	0.015	wt.%			400	1000			C	[58]
70Zr-24.6V-4.5Fe (St-707)	α-Zr + Zr(V,Fe) ₂	Powder		300	10	1 10 ⁻³	300						10	m ³ s ⁻¹ m ²	25	B	[60]
70Zr-24.6V-4.5Fe (St-707)	typically: α-Zr + Zr(V,Fe) ₂	Pellets		350-450	45-60	8.8	-173	0.1	Pa m ³ g ⁻¹	20 -100	10					C	[61]
Zr _x V ₃ Fe (x = 3, 5, 7, 8, 9)	α-Zr + C15-Zr(V,Fe) ₂	Powder		450	30	1	350	1 (x = 9)	wt.%	350	10		0.02	wt.% s ⁻¹	350	C	[62]
Zr _x Ti _{7-x} V ₃ Fe (0 < x < 2.1)	α-Zr + C15-(Ti,Zr)(V,Fe) ₂	Powder		450	30	1	350	1 (x = 0.3)	wt.%	350	100		0.05	wt.% s ⁻¹	350	C	[63]
Ti-Pd coated	bilayered Ti/Pd	Film	1.3 (Ti) / 0.05(Pd)	133	720	4.6 10 ⁻⁶	25						2.8 10 ⁻⁵	m ³ s ⁻¹	133	A	[87]

Ti-Pd coated	bilayered Ti/Pd	Film	1.3 (Ti) / 0.05(Pd)	176	210	1.7 10 ⁻⁷	25					2.3 10 ⁻⁴	m ³ s ⁻¹	176	A	[87]
ZrCoCe-Pd coated	bilayered Zr _{76.2} Co _{20.7} Ce _{3.1} /Pd	Film	2.3(ZrCoCe) / 0.4(Pd)	300	30			1.8	Pa m ³ m ⁻²	25		1	m ³ s ⁻¹ m ⁻²	25	B	[86]
90Ti-10Mo	Powder mixture Ti-Mo	Powder	5	500	10	1 10 ³	400	0.001	Pa m ³	25	1 10 ⁻⁴	1 10 ⁻³	m ³ s ⁻¹	25	A	[64]
92.5Ti-7.5Mo	Powder mixture Ti-Mo	Powder		750	10			4 10 ⁻⁴	Pa m ³ g ⁻¹	25	1 10 ⁻⁴	7 10 ⁻⁹	m ³ s ⁻¹ g ⁻¹	25	B	[66]
80Ti-15Co-5Ce	α-Ti + Ti ₂ Co + Ce oxide	Powder	30	350	30			2.6	wt.%	25	2 10 ³	2.7 10 ⁻³	m ³ s ⁻¹ g ⁻¹	25	B	[32]
Ti-Zr-V	Ti ₃₂ Zr ₁₆ V ₅₂	Film	2	225	1440							0.35	m ³ s ⁻¹ m ⁻²	25	A	[69]
Ti-Zr-V	Ti ₃₀ Zr ₂₀ V ₅₀	Film	5	200	1440	1 10 ⁻¹⁰	25								A	[68]

To satisfy these properties, many alloy getters are multi-phase materials. They often consist of a hydrogen-trapping phase with high storage capacity, such as Ti and Zr, and secondary phases of different chemistries enabling low activation temperatures and fast hydrogenation kinetics. Rare-earth elements can be introduced as secondary phases to readily form very stable oxides promoting the reduction of early transition metals oxides during the activation treatment [31]. Alternatively, intermetallic compounds combining late transition metals, such as Ni and Co, with early transition metals or REs can be used as secondary phases. In this case, they tend to disproportionate upon activation leading to the segregation of catalytic Ni and Co nanoparticles which facilitate dihydrogen dissociation at the getter surface [25,33,34]. Moreover, multi-phase materials favor nanostructuring, lowering activation temperature and enhancing bulk hydrogenation kinetics thanks to a high-density of grain boundaries [26,32,70,72].

The tuning of the getter composition also allows for some applications like isotope recovery, to adapt the equilibrium pressure for reversible desorption at suitable temperature. Kinetic and contaminant tolerance are crucial as these alloys must have very high reactivity with dihydrogen but without interacting with other gas species. Such challenge is difficult to achieve, and various strategies have been developed to solve this drawback. The first one consists of high temperature activation to reduce or dilute native passivation layers formed at the alloy surface. However, this does not prevent reformation of the passivation layer in the presence of gas impurities so that a second way lies in the deposition of a thin (nanometric) protecting layer. Most of the coatings are made of palladium, a metal well known to be hardly oxidized. However, a good linkage of the coating to the bulk material is mandatory and again, chemistry can bring improved adhesive properties by playing with the composition of the layer.

Though the current getter materials bring efficient gettering properties, some new compositions might be developed to get improved trapping. Beside Ti or Zr, other elements (Ca, Y...) forming low equilibrium pressure hydrides exist, and alloying possibilities are extremely rich in the metallic hydride family [96], including emerging concepts such as high-entropy alloys [77,97], leading to possible new materials with enhanced properties. However,

the most important drawback remains the surface state to ensure good sorption efficiency. Beside high temperature activation and metallic coating, other solutions can be proposed. Recently, the embedding of hydride-forming alloys in polymers has been reported [98]. The authors showed that reversible hydride formation in $Mg_{95}Ni_5$ can be achieved without suffering from Mg oxidation by embedding the metallic nanoparticles in a hydrogen permissive/oxygen prohibitive polymer (polymethyl methacrylate, PMMA). Though MgH_2 is not suitable for hydrogen trapping, such concept could be extended to NEG, getting rid of expensive palladium.

Most of the getter market is nowadays focused on ultra-high vacuum pumping systems, micro-electronic-mechanical systems, or recovery of isotopes in nuclear applications. Recently, some other applications have been considered opening new insights for these materials. For example, the mitigation of hydrogen formation by radiolysis or thermolysis in radioactive waste packaging was envisaged by developing hydrogen traps inside the container [24,99,100]. Similarly, to alleviate possible leaks in high pressure storage tank, the addition of Zr_2Fe melt spun ribbons in the outer shell of the reservoir was reported [53]. In the oil industry, the insulation of oil pipes can be improved by ensuring a low concentration of hydrogen in the insulating jacket of the pipeline. Accordingly, new getter materials should be designed to fulfill such complex working conditions and new compositions and composites are foreseen.

Acknowledgement

This contribution honors the memory of my highly respected colleague and friend Michel Latroche who suddenly passed away while the manuscript was under revision.

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