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Retrospect on Zirconium Laves Phases $ZrZn_2$ and $ZrAl_2$ with Their Physicochemical Properties and Perspective for Possible Hydrogen Storage Reactions

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Abstract
The present concise communication emphasizes on two zirconium based AB_2 alloys ($ZrZn_2$ and $ZrAl_2$) with an overview concerning the basic physicochemical properties alongside their structure, elastic, or magnetic nature, with further outlook in hydrogenation application purpose. We started introducing the general aspects of using Zirconium based intermetallics with their advantages and the prevalent apprehension about binary phase diagram of Al-Zr and Zn-Zr systems. We outlined extensive examples overlapping these different properties and we highlighted the importance of hydrogen storage materials in the current worldwide concern about using clean energy.
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1. Introduction

Zirconium alloys are known to have a good corrosion resistance and its incorporation in intermetallic alloys or adjunct substitution provides improved protection against oxide growth depending on alloying concentration (Féron, 2012; Samaras, 2011). This makes Zr-based alloys valuable for different applications like solid-gas reactions or others hydrothermal energy conversions (Mine et al., 2014; Kumarn et al., 2013; Lototskyy et al., 2018; Matsuyama et al., 2018).

Binary phase diagram of Zr-Zn and Zr-Al systems were reported since 1992 in the Phase Equilibria Journal (Dutkiewicz; Murray et al.). In 2001 thermo-chemistry modeling groups start developing further database series including wide range of optimized phase diagrams (Example in Figure 1) combining several thermodynamics computing solutions such as the FactSage modules (Bale et al., 2009; Harvey et al., 2012).

2. Solid-state and Physicochemical Properties

Physical properties of $ZrZn_2$ compound have been reported with considerable emphasize on its magnetic measurements. Carrington et al., (2005) shows ferromagnetic character of the material and temperature dependence through magnetization isotherms giving important information about spin fluctuations in $ZrZn_2$ matrix. Other magnetism or transport properties were reported and shows that $ZrZn_2$ spark erosion can proceed a superconducting surface layer on the bulk material (Yelland et al., 2005). Supplementary detailed measurements have been investigated also at high pressure to establish electronic topology on $ZrZn_2$ Fermi surface, interestingly meta-magnetic behavior is observed at a critical point (Kabeya et al., 2013).

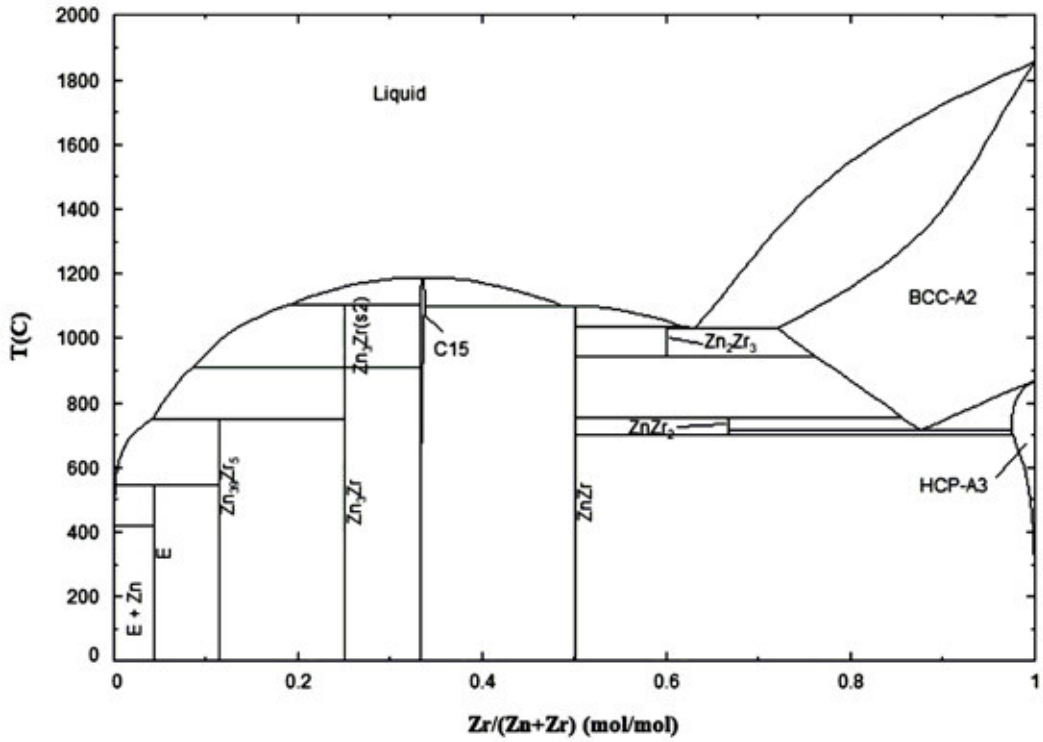

Figure 1. Example of binary phase diagram given by FactSage (Zn-Zr system)

Magnetic study of $ZrAl_2$ was reported in literature investigating the influence of rare earth impurities ($Zr_{1-x}RE_xAl_2$) on its resistivity and magnetic susceptibility. It was found some unexpected results consisting in resistivity increment related to the fractional valence (Hafez and Slebarski, 1990).

ZrAl2 crystallizes in the C14 hexagonal Laves structure shown in Figure 2a, with lattice constant a=5.282 Å and c=8.748 Å. ZrZn2 crystallizes in the C15 cubic Laves structure shown in Figure 2b, with lattice constant a=7.393 Å and the Zr atoms in this case form a tetrahedrally coordinated diamond structure.

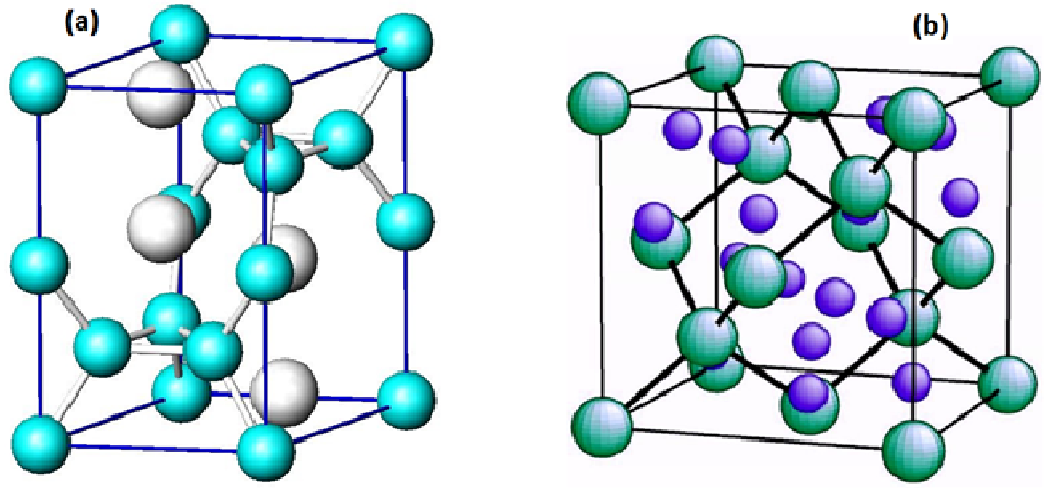

Figure 2. (a) The C14 Laves Phase structure of $ZrAl_2$ (Hexagonal $P6_3/mmc$) Zr atoms larger spheres (white)
(b) The C15 Laves Phase structure of $ZrZn_2$ (Cubic Fd-3m) Zr atoms larger spheres (green)

$ZrZn_2$ elastic constant increases linearly with the compression pressure and the compound is stable up to 60 GPa. First-principle study based on functional density energy calculation confirmed the mechanical behavior of the compound for low and high temperature (Sun et al., 2014).

Mechanical properties assessment of $ZrAl_2$ (elastic constants and deformation mode) have been reviewed recently exhibiting low elastic anisotropy with substantial temperature effect on linear thermal expansion for low pressure (Zhang et al., 2014).

Hydrogenation experiments on $ZrAl_2$ show scarce absorption. However, $Zr(Al_{0.5}Co_{0.5})_2$ composite performed acceptable capacity of 1.1 H/M (Jacob et al., 2011).

Partial substituted compounds $ZrZn_{2-x}Al_x$ have been investigated by X-ray powder diffraction: $ZrZn_{1.5}Al_{0.5}$

is Pm3m cubic phase, but $ZrZn_{0.5}Al_{1.5}$ sample is giving same C15 Lave phase configuration as the non-substituted $ZrZn_2$ alloy.

The unit cell parameter of the sample $ZrZn_{0.5}Al_{1.5}$ is a = 7.473 Å and was synthesized using classical high temperature annealing silica tube (Drašner and Blažina, 1981).

3. Outlook towards reverse hydridable materials

Complex Zr-based AB_2 alloy ($ZrNi_{1.2}Mn_{0.48}Cr_{0.28}V_{0.13}$) was studied as catalyst of gas-diffusion electrodes within alkaline-fuel cell giving moderate hydrogen-diffusion at current density of 40-60 mA/cm^2 (Hu et al., 2004). Similar multi-element or high-entropy Zr-alloys were produced recently by sophisticated heat treatment process resulting slight or substantial improvement in hydriding behavior (Kim 2009; Zhang 2013; Wu 2015; Karlsson 2018; Zlotea 2019; Young 2015; Davidson 2003).

However, a series of $ZrFe_x$ alloys with different iron composition range were achieved using a conventional arc furnace with inert Argon. Hydrogen desorption isotherms were elaborated and maximum hydrogen capacity of 1.2 H/M (1.80 wt % H_2) was obtained for optimum $ZrFe_{1.9}$ (Sivov et al., 2011). This shows that we can get in specific cases an efficient sorption and enhanced capacity by using easy simple substitution with a transition periodical element.

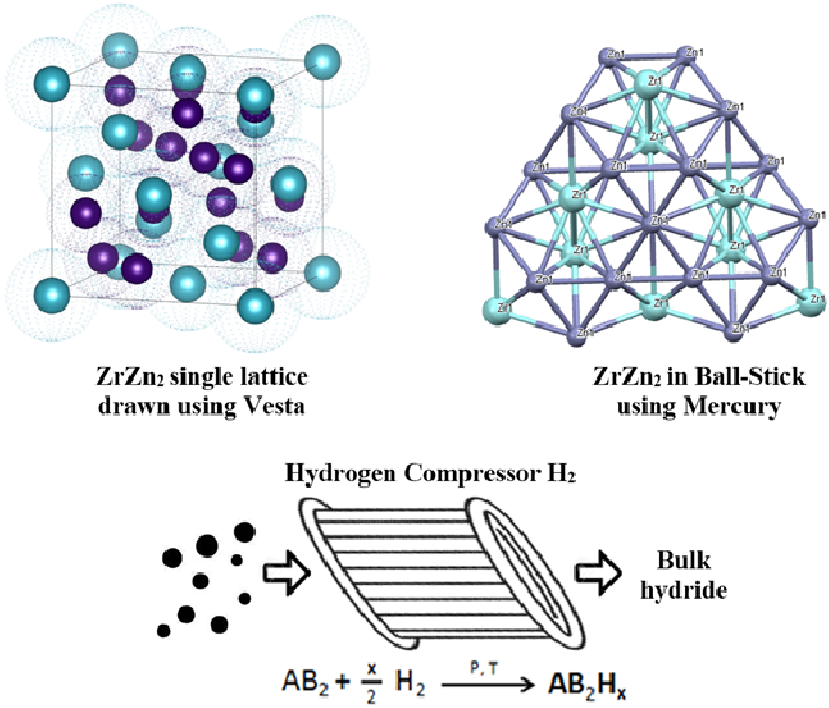

Figure 3. Possible bulk hydrides formation using high pressure hydrogenation system

In this current account $ZrZn_2$ and $ZrAl_2$ Laves phases exhibit very attractive and interesting physicochemical properties, as an insight of appropriate matrix substitution (considering suitable metal substitute $ZrB_{2-x}M_x$, B = Zn or Al, and M = Cobalt, Copper or/and Manganese) is particularly contributing in emerging advanced reversible HSA hydrogen storage nano-materials (Figure 3). We are involved in our laboratory framework in developing new Zirconium based AB_3 alloys like $CeZr_2Ni_5Cr_4$ and $LaZr_2Ni_5Cr_4$ having interesting hydrogenation properties particularly the electrochemical storage in Nickel-Metal Hydride Batteries Ni-MH (Sahli et al., 2017, 2016). We are also seeking recently to substitute and replace toxic Chromium using other more sustainable elements (Jaafar et al., 2020, 2018; Slama et al., 2019).

4. Conclusion

We have overviewed in this article the general properties of two interesting binary Laves phases $ZrZn_2$ and $ZrAl_2$. These two intermetallics compounds were described and inspected in terms of structural and physico-chemical characteristics exhibiting both good mechanical and superconducting behavior at various temperature offering hands-on many energy storage purposes as well others possible high temperature conversion reactions. Our ongoing efforts in the laboratory are handled in further development and contributions optimizing these AB_2 alloys by introducing other metal substitutions or combination with AB_5 compounds giving exclusively novel hydrogen-storage materials.

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