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Can reduced size of metals induce hydrogen absorption: $ZrAl_2$ case

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ABSTRACT

The hydrogen absorption ability of the non-absorbing Al-rich $ZrAl_2$ compound was examined after reducing its particles-size to the nanometer regime. The hydrogen abstinence of bulk $ZrAl_2$ has been previously related to its excessive elastic shear stiffening. The particle size of $ZrAl_2$ was reduced by attrition milling and cryomilling. The minimal average particle size was estimated from powder X-ray diffraction analysis to be in the range of 10–20 nm. The hydrogen absorption of the milled compounds was measured in different hydrogenation systems at hydrogen pressures between ~6 MPa and ~2 GPa. In all the cases the hydrogen absorption was negligible. In addition, there was a reduction of the hydrogen absorption capacity of nanosized $Zr(Al_{0.5}Co_{0.5})_2$ as compared to the corresponding bulk compound at the same conditions. We suggest, in view of our and other results, that no significant improvement of the thermodynamics (unlike the kinetics) of the hydrogen absorption can be achieved via the nanoparticle avenue.

1. Introduction

Hydrogen storage is a critical issue for establishing a hydrogen economy society [1]. The requirements for good hydrogen absorbers and the present state of art are summarized in a recent paper [2]. Despite the considerable efforts during the last 30 years, the desired hydrogen absorber for mobile applications has not been found yet. Light elements, like Al, Li, etc., should be a major component in a hydrogen-absorbing compound, in order to achieve high H-weight percentage. In the present work we examine the possibility to trigger hydrogen absorption in the non-absorbing $ZrAl_2$ compound by reducing the compound particle size to the nanometer region. $ZrAl_2$ is a member of the anomalous hydrogen absorbing systems $Zr(Al_xCo_{1-x})_2$ and $Zr(Al_xFe_{1-x})_2$, $1 \geq x \geq 0$ [3,4]. The quenching of hydrogen absorption for large x values in these systems is in apparent correlation with enhanced shear stiffening of the parent compounds. This enhanced shear stiffening has been interpreted to inhibit the attractive hydrogen–hydrogen interaction and thus prevent the Al-rich compounds from forming hydrides [4]. A possible way to change the elastic properties of matter is by reducing its particle size to the nanometer regime. There have been reports that this procedure may cause either elastic stiffening or softening [5,6]. In addition to $ZrAl_2$, we examined the influence of the particle size on the hydrogen absorption capacity of $Zr(Al_{0.5}Co_{0.5})_2$. This compound absorbs hydrogen, though significantly less than the $Zr(Al_xCo_{1-x})_2$ compounds with $x \leq 0.25$, and its hydrogen capacity seems susceptible to variations of its elastic properties.

2. Materials and methods

$ZrAl_2$ and $Zr(Al_{0.5}Co_{0.5})_2$ were prepared by arc melting several times the weighed pure (99.9% or better) elemental constituents. The crystal structures of the compounds were confirmed by X-ray powder diffraction. The melted pellets were crushed to powder, which was repeatedly crushed and transferred through metal sieves, until particles of size below 50 μm (−50 μm) were obtained. These powders were further used for attrition, cryogenic milling or ball milling under hydrogen atmosphere. The attrition was performed in ethanol with stainless steel balls. The maximum attrition times were 8 h for $Zr(Al_{0.5}Co_{0.5})_2$ and 12 h for $ZrAl_2$. After the attrition, the powder was dried in ambient room atmosphere, carefully and gradually in order to prevent its ignition. The amount of powder, used for each one of the attritions, was about 100 g.

The cryogenic milling (cryomilling) was performed for 2 g batches in a Spex 6750 Freezer mill. It consists of a polycarbonate centre cylinder (vial) having two stainless steel ends and a stainless steel impactor, able to collide back and forth against these two ends. The vial is filled with the powder to be cryomilled and then immersed in a liquid nitrogen bath. Four powders were cryomilled: I – $ZrAl_2$, previously attrited for 12 h; II – $Zr(Al_{0.5}Co_{0.5})_2$, previously attrited for 8 h; III – as cast $ZrAl_2$, crushed to −50 μm; and IV – as cast $Zr(Al_{0.5}Co_{0.5})_2$, crushed to −50 μm. These powders were handled in ultra high purity Ar glove box (<1 ppm O_2 and <1 ppm H_2O), and were cryomilled for 4 h each one, at an impact frequency of 30 Hz.

Diffractograms of all the powders were carried out in air, utilizing Philips 1050/70 powder diffractometer, operating at a power of 40 kV and 30 mA, with

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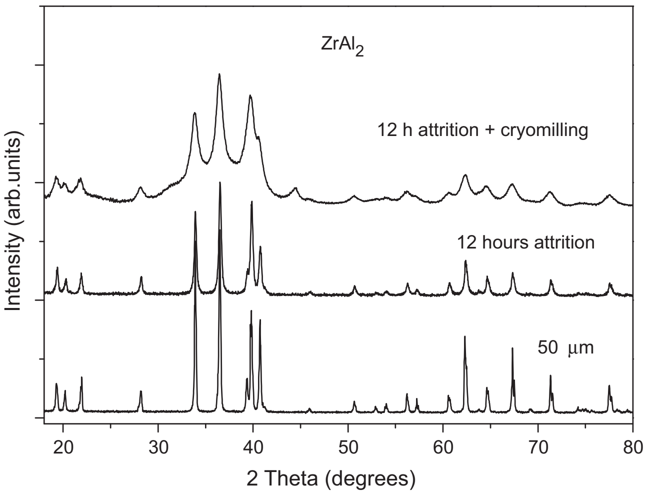

Fig. 1. X-ray diffraction patterns of $ZrAl_2$ for differently treated powders, as indicated in the figure.

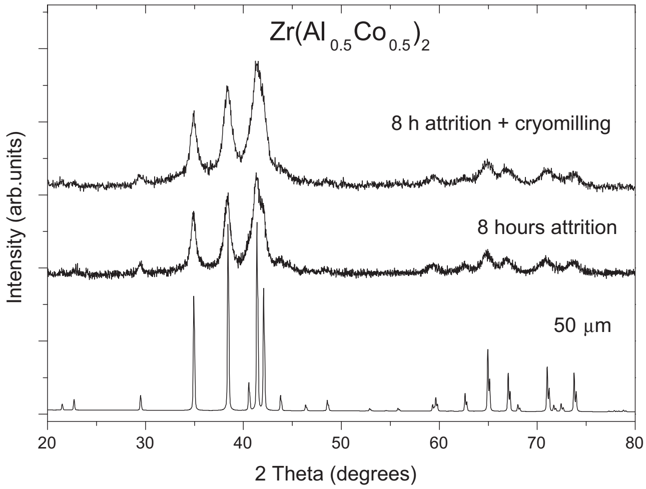

Fig. 2. X-ray diffraction patterns of $Zr(Al_{0.5}Co_{0.5})_2$ for differently treated powders, as indicated in the figure.

Bragg-Brentano focusing geometry and a long fine focus, Cu anode tube and reflected beam graphite monochromator. The Ar-treated cryomilled powders, sealed into quartz capillary tubes, were examined also at the Swiss-Norwegian Beam-Line (SNBL, BM01A station, 0.7147 Å wavelength) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The grain size and the microstrain of the powders were obtained by analyzing the integrated widths of X-ray diffraction peaks by the Williamson-Hall (WH) procedure [7]. The WH approach considers the case where the pure physical integral width, β, of the experimental peak consists of two contributions: one is due to the grain size and can be expressed according to the Debye–Scherrer equation as $\lambda/\langle D\rangle \cos\theta$ and the second is caused by the lattice deformation and is expressed as $4\varepsilon\tan\theta$. After some simple mathematical manipulation the expression for the integral width β may be written in the form:

$$\beta \quad \cos \quad \theta = \frac{\lambda}{\langle D\rangle} + 4\varepsilon \quad \sin \quad \theta$$

where $\langle D\rangle$ is the average grain size, ε is the elastic strain, λ is the X-ray wavelength and 2θ is the scattering angle. From a plot of $\beta\cos\theta$ vs. $\sin\theta$ one can evaluate the contributions of strain and grain size to the XRD line broadening. The particle size of some of the powders was estimated also from their surface areas, measured by Brauner–Emmett–Teller (BET) nitrogen adsorption isotherms, and from known X-ray mass densities [8]. Some transmission electron microscope (TEM) pictures were obtained with 100 kV electrons in the Tecnai 12 TWIN TEM.

Hydrogen uptake up to 20 MPa was checked up in Sieverts-type, pct (pressure–composition–temperature) systems. Exposure to hydrogen was done at room temperature. The reactor, containing the metal powder, was subsequently heated for possible activation to temperatures not exceeding 300 °C, in order to avoid hydrogen diffusion through the 316L stainless steel reactor walls. X-ray diffractograms of hydrogen-exposed samples were occasionally run after removing them from the hydrogenation system. It was necessary to use Si reference in order to account for small possible shifts in the position of the diffraction peaks with regard to the corresponding original intermetallic samples before exposing them to hydrogen.

Hydrogenation experiments at pressures up to 2 GPa and temperatures below 150 °C were carried out in a piston-cylinder high pressure system [9]. The samples were usually kept under high hydrogen pressure for one to few days. Before discharging the sample from the system, it was cooled to −60 °C and then immersed into liquid nitrogen until X-ray diffractograms were run. The presence of a hydride phase was indicated by a shift in the positions of the diffracted peaks to smaller angles, relatively to those of the original compound. The amount of absorbed hydrogen was determined from the difference between the crystal volumes of the samples before and after hydrogen exposure, utilizing the value of 2.6 $Å^3$/(H atom) for the $Zr(Al_xCo_{1-x})_2$ system [8].

The attrited $Zr(Al_{0.5}Co_{0.5})_2$ and −100 µm $ZrAl_2$ powders were exposed to hydrogen pressure of about 8 MPa during ball milling in a Fritsch P6 planetary mill in a specially designed stainless steel vial. More experimental details are given in a previous publication [10]. The ball milling was carried out at 400 rpm for 20–100 h. The vial was cooled at the end of the experiment and the samples were examined by X-rays.

3. Results

Figs. 1 and 2 present the X-ray diffraction of $ZrAl_2$ and $Zr(Al_{0.5}Co_{0.5})_2$ for the different particle size-reducing procedures. The significant broadening of the X-ray lines is associated with the decrease of the grain size caused by the milling procedures. Table 1 summarizes the results for particle sizes as determined from the XRD and BET analyses. TEM pictures of attrited and then cryomilled $ZrAl_2$ powder are shown in Fig. 3. The particles seem to be in the form of flakes of about 10 nm thickness. This shape may indicate some kind of anisotropy.

Hydrogenation experiments of $ZrAl_2$ were performed for 55 nm particles at 6 MPa and at 0.7, 0.8, 1 and 2 GPa, and for 15 nm particles at 6 and 20 MPa. In all these cases the hydrogen absorption, observed either in the hydrogenation system or in the subsequent X-ray examinations was negligible.

Hydrogenation experiments of $Zr(Al_{0.5}Co_{0.5})_2$ were performed for 25 nm attrited particles at 6 MPa and at 0.8 GPa. $Zr(Al_{0.5}Co_{0.5})_2$ absorbed about 0.8 H atoms per formula unit (f.u.) at 6 MPa. This is about 20% less than 1.05 H atoms/f.u., observed previously at 6 MPa for bulk $Zr(Al_{0.5}Co_{0.5})_2$ [8]. The same, 25 nm sample absorbed about 1.1 H atoms/f.u. at 0.8 GPa.

ZrH_x was identified in the $ZrAl_2$ and $Zr(Al_{0.5}Co_{0.5})_2$ X-ray diffraction patterns taken after the hydrogen ball milling (HBM) procedures, i.e. disproportionation has taken place during the HBM. These experiments were not continued.

Table 1
Particle size (PS), grain size (GS) and microstrain, ε, attained after attrition, attrition and cryomilling and cryomilling alone in $ZrAl_2$ (I and III) and $Zr(Al_{0.5}Co_{0.5})_2$ (II and IV) compounds.

Technique	Attrition		Attrition +Cryomilling		Cryomilling	
	$ZrAl_2$ 12 h	$Zr(Al_{0.5}Co_{0.5})_2$ 8 h	I	II	III	IV
BET surface area [m^2/g]	5.8	12				
BET PS [nm]	∼225	∼80				
XRD GS [nm]	55 ± 5	25 ± 3	14 ± 3	12 ± 3	15 ± 2	39 ± 3
XRD $\varepsilon \times 10^3$	0.7 ± 0.3	5.5 ± 1	5.5 ± 1	4 ± 1	6 ± 1	9 ± 1
Synchrotron GS [nm]			9 ± 2	17 ± 3	16 ± 3	34 ± 5
Synchrotron $\varepsilon \times 10^3$			4 ± 1	9 ± 2	8 ± 2	13 ± 2

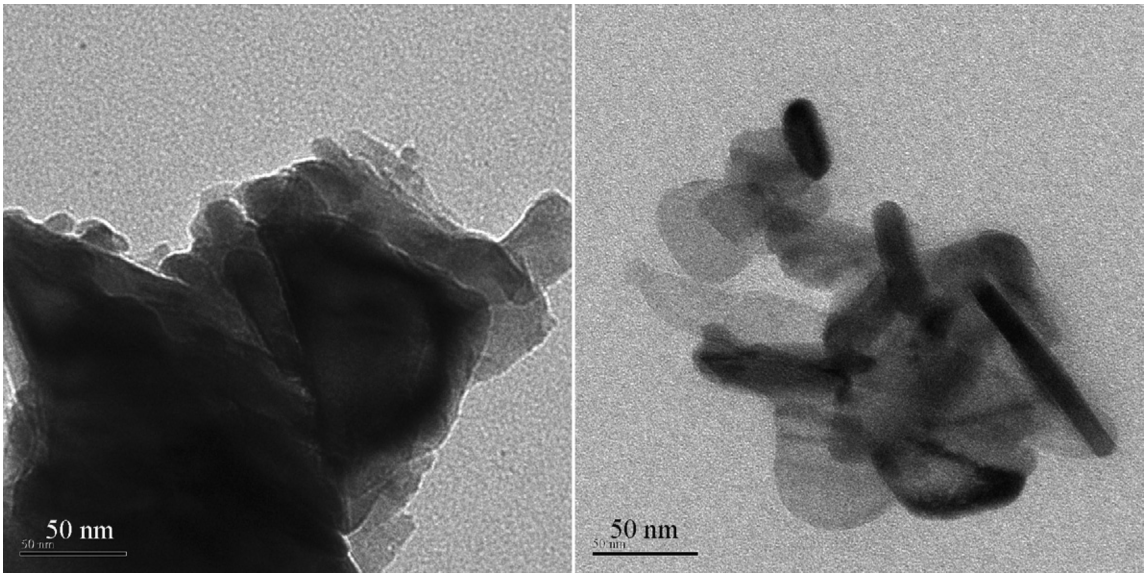

Fig. 3. Transmission electron micrographs of initially attrited $ZrAl_2$ after 4 h of cryomilling. On the left side there is an agglomerate of particles. On the right side details of separate particles can be observed.

4. Summary and discussion

$Zr(Al_{0.5}Co_{0.5})_2$ compounds were more compliant to reducing their particle size by attrition than $ZrAl_2$. This is probably associated with the different elastic properties of the two compounds. $ZrAl_2$ has significantly larger shear modulus and it is thus much stiffer than the $Zr(Al_{0.5}Co_{0.5})_2$ compound [4]. Cryomilling was more efficient in reducing the particle size of attrited $ZrAl_2$, but did not change much in the case of attrited $Zr(Al_{0.5}Co_{0.5})_2$. The minimum grain size, achieved in the present study, was about 15 nm. As could be expected, the particle sizes, observed in TEM and derived from the BET measurements, are larger than the corresponding values analyzed from the diffraction results.

The hydrogen absorption in all the $ZrAl_2$ powders, studied in the present work, was negligible, even at hydrogen pressure in the GPa range, while $Zr(Al_{0.5}Co_{0.5})_2$ has demonstrated decreased hydrogen absorption ability with the decrease of grain size to the nanometer region. It is of interest to consider the present results in view of some observations in nanosized metals and metal layers. Lamber et al. have observed a significant decrease of the lattice constants for Pd particles below 5 nm, and referred to the absence of hydride formation for particles less than 2.6 nm [11]. Kirchheim has reported a significant narrowing of the metal-hydride plateau region in Pd upon reducing the Pd cluster size from 6 to 3.6 nm [12]. A recent study of hydrogen absorption in Mg thin layers has demonstrated a very significant increase of the hydrogen plateau pressure as the Mg thickness is reduced from 40 to 10 nm [13]. The latter observation has been explained in terms of the hydrogen–hydrogen long range elastic interaction and the clamping of the Mg layers. We believe that in all the mentioned cases, including the present study, the hydrogen absorption behavior is determined by this elastic interaction. We suggest that the elastic constants of the nano-$ZrAl_2$ and $Zr(Al_{0.5}Co_{0.5})_2$ change in a way that further decrease the hydrogen–hydrogen attraction in the nanomaterials with regard to their bulk counter partners. We thus propose that no improvement of the thermodynamic properties (both capacity and plateau pressure) of transition metals and alloys, which tend to expand upon hydrogen absorption, can be achieved by mere reducing the particle size.

Acknowledgments

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