Short communication

Hydrogen production and storage—Investigation of Hf-based intermetallics

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ABSTRACT

Hafnium-based intermetallics Hf_2Fe, Hf_2Co and Hf_2Ni are investigated as hydrogen absorbers at atmospheric pressure and their electrocatalytic activities are compared. The absorption process is carried out in typical volumetric apparatus. Their crystal structures and morphological characteristics are investigated by X-ray difractometry (XRD) and scanning electron microscopy (SEM). According to the absorption abilities, the investigated intermetallics can be ordered as follows: $Hf_2Fe > Hf_2Co > Hf_2Ni$.

Ab initio calculations, within the framework of the density functional theory (DFT), as implemented in the full-potential (linearized) augmented plane-wave (FP/LAPW) method, confirms the experimental investigations. The calculations are important as a way of predicting the best cathode and storage materials.

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1. Introduction

Hydrogen is a promising renewable, secondary energy source. The electrolytic hydrogen production using numerous transition metals intermetallics as cathode materials and their hydrogen absorption capabilities are widely investigated in order to find the best electrocatalysts and hydrogen storage materials.

Hydrogen production *via* water electrolysis promises to be of a great future importance. Due to the high energy consumption $(4.5–5\,kWh\,(m^3{}_nH_2)^{-1})$, only about 10% of all methods for hydrogen production belong today to the electrolysis. The improvement of hydrogen economy implies a necessary reduction of this energy consumption, which, amongst the other approaches, includes finding an advanced combination of metals as cathodes in the electrolysis. The catalytic activity for hydrogen evolution reaction (HER) of various metals and alloys is caused by their d-electronic configuration. The bonding effectiveness, and consequently the electrocatalytic activity, exhibits typical volcano plots with maximum at nearly filled d-orbital, at about d^8-electronic configuration [1–3]. Brewer's high-temperature thermodynamics [4–6] suggests that whenever metals from the left-half of the transition series, having empty or half-filled d-orbital are alloyed with metals from the right-half of the transition series, having internally paired d-electrons not available for bonding in pure metals,

it results in approximate optimal d-electronic configuration and in rather strong bonding, and consequently in good electrocatalytic activity. But, the optimum in electrocatalytic activity appears at neither too strong nor too weak bonding, but at the moderate values in between.

One of the limitation connected with the exploitation of hydrogen as a fuel is the difficulty in storing it economically and conveniently. At the present, hydrogen is stored as a compressed gas or as a cryogenic liquid. Gaseous storage requires a large volume and/or weight of storage vessels, while liquid hydrogen requires rather expensive liquefaction process and energy consumption as well.

Hydrogen in metals has been a subject of wide and universal importance for about a hundred years, and remains in the focus of various investigations today. Metal hydrides are widely investigated [7,8] in order to evaluate the scope of their application in hydrogen storage devices. Hf_2Fe, Hf_2Co and Hf_2Ni have been investigated as systems interesting for hydrogen storage, since they are able to form hydrides in hydrogen–metal atom ratios $H/M \geq 1$ at rather high temperatures and high pressures $(>1\,kPa)\,(T \approx 3000\,°C)$ [7].

Since during the hydride formation [9] the adsorbed hydrogen atoms (H_2, ad) penetrate into the bulk and form the nuclei of hydride phase, the main concern is to improve the solubility of hydrogen in metals as potential hydrogen storage materials.

Metal and alloys intended to serve as hydrogen storage media must provide for the hydriding/dehydriding procedure to be reversible and to occur at a hydrogen partial pressure as close

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as possible to the atmospheric one. It is also important that the metals and alloys, after a great number of hydriding/dehydriding cycles, maintain their physicochemical characteristics unchanged. In particular, it is important that their particle sizes, phase composition and hydriding capacity remain unchanged [10]. Up to now, there have been no metals or alloys which completely satisfy such requirements. As is commonly known, hydrogen absorption alloys are mainly intermetallic compounds consisting of hydride forming metals such as 2A, 3A or 4A group elements and hydride non-forming metals such as 7A or 8A group elements. The non-hydrideable component mechanically stabilizes the alloy structure, reducing, on the other hand, the total hydriding capacity to some extent [11].

It was proposed [12] that for transition metal alloys, the interaction energy is controlled by a mechanism similar to the Miedema's "reverse stability" rule, i.e., the larger is the binding energy of the alloys, the stronger is the repulsion between the alloying atom and hydrogen. It was suggested that intermetallic compounds with calculated heats of hydride formation (ΔH) (metal–hydrogen systems with dissociation pressures of about 1 bar, around the room temperature) in the range from -40 to -15 kJ mol^{-1} H, are of the practical interest as potential hydrogen storage alloys [13].

In the present work, the kinetics of hydrogen absorption in Hf$_2$Fe, Hf$_2$Co and Hf$_2$Ni was investigated in the temperature range from 573 to 823 K, under the constant hydrogen pressure of 1 bar. We also provide for a comparison with their behavior as cathode materials, investigated in our previous work [14]. We complement all our experimental results with *ab initio* calculations.

2. Experimental

The intermetallic phases were prepared from high purity components in RF induction furnace under a very pure argon stream and remelted several times. The alloy's composition and their structure types were confirmed by powder X-ray diffractograms in our previous studies [15–17].

The experimental investigations of the Hf-based alloys, as cathode materials, and theoretical calculations that confirmed their electrocatalytic activities were described elsewhere [14,18,19].

After grinding, hydriding and dehydriding were carried out in typical volumetric equipment [20]. A quartz tube containing a weighed quantity of the sample powder (about 100 mg) was inserted into a thermostated tube furnace. The sample container was connected to vacuum equipment and a hydrogen reservoir by a set of valves. Before use, each sample was pretreated by annealing at 873 K (600 °C) for 2 h under a vacuum of 1×10^{-3} mm Hg. In the present work, the hydrogen absorption and desorption experiments were carried out in a constant volume system. After hydriding, dehydriding was done under the same conditions as a pretreatment. Starting always with the hydrogen pressure equal to the atmospheric one, the amount of absorbed hydrogen as a function of time was calculated on the basis of pressure drop. The experimental conditions were isobaric as the relative pressure drop never exceeded 5%.

After pretreatment, samples were subjected to the multiple hydriding/dehydriding cycles. Ultrapure hydrogen was introduced into the system under the pressure of 1 bar (the initial hydrogen pressure) for each experiment. The hydriding reaction was carried isothermally; within the temperature range 573–823 K (300–550 °C) for Hf$_2$Ni and Hf$_2$Co and within the temperature range 348–573 K (75–300 °C) for Hf$_2$Fe. Hf$_2$Fe was hydrated at lower temperatures because of hydride decomposition at higher temperatures [21].

The pressure change due to the absorption was continuously measured by means of a capacitance manometer until thermodynamic equilibrium was attained at the given temperature.

Table 1
Energy consumption (Q) in HER reaction (intermetallic used as cathode materials, $i = 40$ mA cm^{-2} and $T = 323$ K); Activation energy (E_a) in hydrogen absorption process (intermetallics used as absorbers, hydrogen pressure 1 bar); calculated enthalpies of formation (ΔH_f) of intermetallics.

Intermetallic	Q (kJ mol^{-1})	E_a (kJ mol^{-1})	ΔH_f (kJ mol^{-1})	ΔH_f [a] (kJ mol^{-1})
Hf$_2$Ni	–	34.59	–	−46
Hf$_2$Co	254.4	19.62	−31.8	−38
Hf$_2$Fe	280.0	2.74	−20.3	−23

[a] Ref. [20].

3. Results and discussion

3.1. The electrocatalytic activity

Stable Hf-based alloys, Hf$_2$Fe, Hf$_2$Co and Hf$_2$Ni, have been investigated as cathode materials for hydrogen production from alkaline solutions and compared with commercial electrodes [19]. These intermetallics belong to the group of binary systems formed between hypo-d-transition (Hf) and hyper-d-transition metals (Fe, Co and Ni) and, on the basis of Brewer's high-temperature thermodynamics mentioned above [4–6], gives optimal d-electronic configuration (d^8) and rather strong bonding for good electrocatalysts.

The order of the electrocatalytic activity that originates from the obtained energy consumption of the investigated cathodes materials is the following: Hf$_2$Pd > Hf$_2$Co > Hf$_2$Fe > Fe > Ni. The energy consumption for the electrolytic hydrogen evolution process as a measure of the electrocatalytic activity of electrode materials at 40 mA cm^2 and 323 K is presented in Table 1. It can be seen that the energy consumption for Hf$_2$Co is smaller than that of Hf$_2$Fe and thus Hf$_2$Co is better electrocatalyst than Hf$_2$Fe.

3.2. The absorption ability

The absorption of hydrogen, using Hf-based intermetallics, was investigated at four different temperatures as 823, 723, 673 and 573 K (Hf$_2$Ni and Hf$_2$Co) and at 573, 473, 423 and 348 K (Hf$_2$Fe).

The pressure change was measured during the time and after that the number of hydrogen moles absorbed into 1 mol of intermetallic (H/M) was calculated on the basis of the ideal gas equation.

The experimental data were fitted by exponential equation of the following type:

$$y = a(1 - e^{-bx})$$

As an example, the exponential curves that fitted the experimental data for the first hydrating cycle obtained at 523 K are presented in Fig. 1.

The interpretation of kinetic data was attempted on the basis of equation:

$$\frac{dx}{dt} = k_1 p_{H_2}^{1/2}(a - x)$$

where a is the equilibrium (maximum) amount of H/M and x represents H/M for time t. Integrating this equation assuming that $k = k_1 p_{H_2}^{1/2}$, as the hydrogen pressure is practically constant, always close to 1 bar, one obtains:

$$k = \frac{1}{t} \ln \frac{a}{a - x}$$

This equation predicts the linear dependence of $\ln(a/a - x)$ vs. time with the slope k, i.e. the rate constants at the given temperature. Those plots for all investigated alloys are given in Fig. 2 and the rate constants obtained are presented in Table 2.

The rate constants plotted as a function of reciprocal temperature, according to Arrhenius equation (Fig. 3), give activation
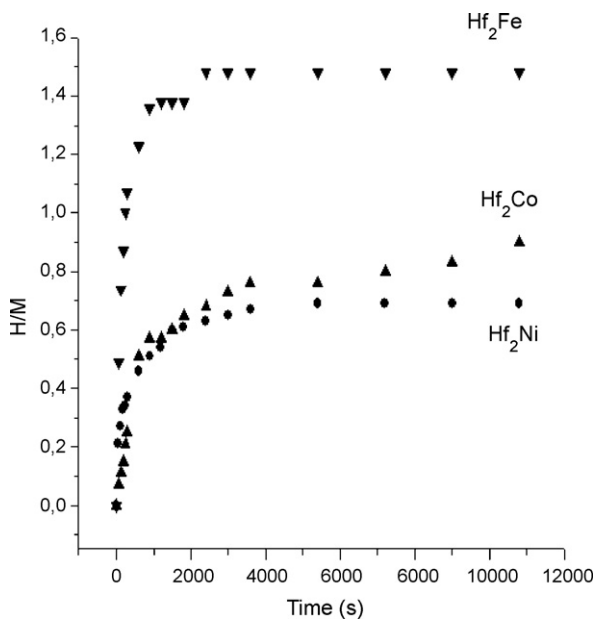
Fig. 1. The average H/M values as a function of time for Hf_2Fe, Hf_2Co and Hf_2Ni at 573 K; the experimental data fitted by exponential equation of the type $y = a(1 - e^{-bx})$.
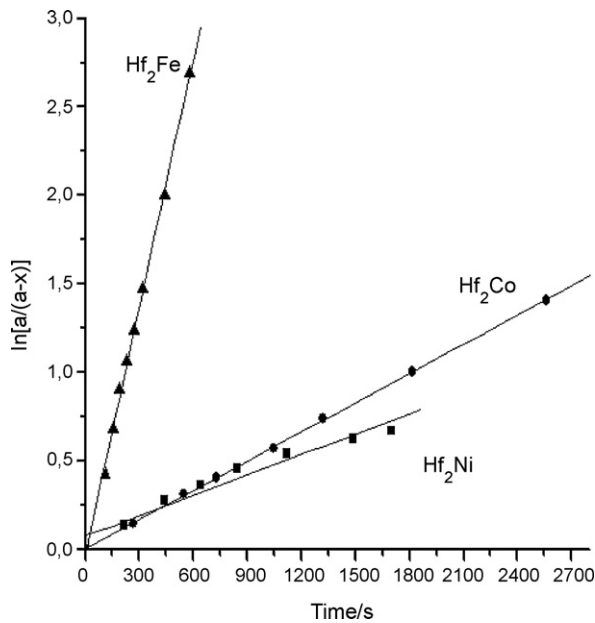

Fig. 2. The dependence of $\ln[a/(a-x)]$ vs. time at 573 K; a is equilibrium (maximum) amount of H/M (hydrogen atoms absorbed per one molecule of alloy) and x is H/M for time t.

Table 2
The temperature dependent hydriding capacity (H/M max) and rate constants for the investigated intermetallics.

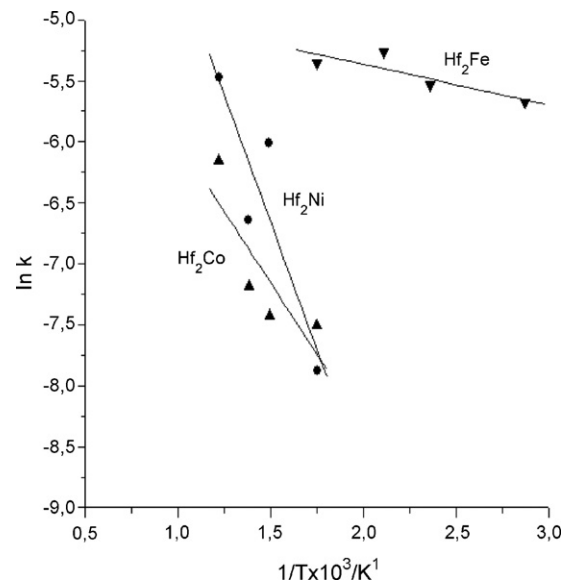|	H/M max			$k \times 10^3$ (s^{-1})		
	Hf_2Ni	Hf_2Co	Hf_2Fe	Hf_2Ni	Hf_2Co	Hf_2Fe
348	–	–	2.00	–	–	3.43
423	–	–	2.21	–	–	3.96
473	–	–	2.05	–	–	5.18
573	0.69	0.90	1.48	0.38	0.55	4.72
673	0.95	1.11	–	2.46	0.60	–
723	1.13	1.04	–	1.31	0.76	–
823	0.92	0.93	–	4.20	2.12	–

Fig. 3. The dependence of rate constants vs. reciprocal temperature of hydriding process (Arrhenius plots).

energies for the hydriding process of the investigated intermetallics. Arrhenius plots are given in Fig. 3 for all three intermetallics investigated in this work. The obtained values of activation energy are given in Table 1.

3.3. Ab initio calculations

It is very well known that, in general, the electrocatalytic activity correlates strongly with the stability of a certain intermetallic compound. In order to roughly estimate the stability of the investigated intermetallics, *ab initio* calculations of their formation enthalpies were performed [18] and presented in Table 1. From calculated values of formation enthalpies, it can be noticed that Hf_2Co is more stable than Hf_2Fe. The greater stability of Hf_2Co is also indicated by the calculated electron density at Fermi level $N(E_F)$ which values, given per formula unit (f.u.), arround Fermi level (E_F) are 2.16 and 2.06 states/eV f.u. for of Hf_2Fe and Hf_2Co, respectively.

It can be argued that the formation enthalpies of the alloys are correlated with the formation energy of the hydrides, in such a way that if the alloy is more stable the corresponding hydride would be less stable [22,23] and therefore the efficiency of electrocatalysis
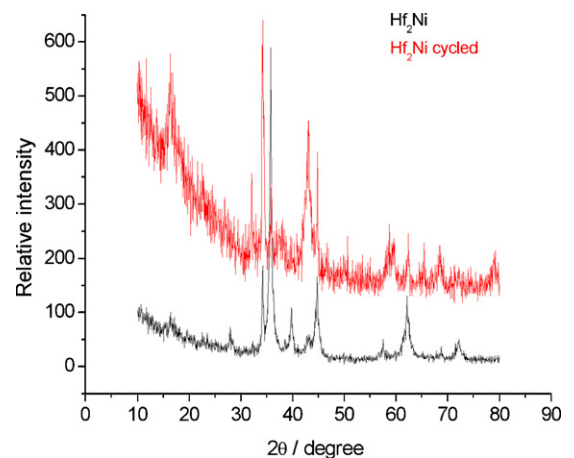

Fig. 4. XRD spectrum of Hf_2Ni intermetallics: (a) before hydrogen absorption (bottom) and (b) after 20 cycles of hydriding/dehydriding at 673 K.

would be greater. In this sense our calculations reproduce the experimental trend.

On the basis of structural investigation by XRD spectroscopy, it could be concluded that the lattice structure was not changed during the hydriding process. There is no phase transformation, although hydrogen atoms dissolved interstitially induces the lattice expansion. The investigation of morphological characteristics by SEM before and after hydrogen absorption pointed that the average dimensions of the particles were not changed. However, the expected small splits, due to the hydriding process, could be seen using the larger amplification [24]. As an example, XRD spectra and SEM micrographs of Hf$_2$Ni powder before and after the 20 performed cycles of hydrogen absorption/desorption at 673 K are presented in Figs. 4 and 5. It could be concluded that, as expected for simple hydride forming alloys [20], the partial decomposition

of the alloy occurs during cycling. However, the lattice parameters of the remaining Hf$_2$Ni were maintained. The SEM micrographs of Hf$_2$Ni powder pointed out that after 20 absorption/desorption cycles the average particle diameter (7 μm) was apparently not affected. However, numerous cracks appear along the particles, which are particularly visible under the amplification 2000, as a known consequence of the repetition hydriding/dehydriding cycles [20]. These considerations are important in the possible usage of Hf-based intermetallics as hydrogen storage materials.

On the basis of the results obtained in this work it follows that Hf-based intermetallics could be used as cathode material in HER reaction with more preferable performances than commercial cathodes (Fe, Ni). Hf$_2$Co is better electrocatalyst than Hf$_2$Fe because of its smaller energy consumption (Q) in the electrolytic hydrogen production as a consequence of its higher enthalpy of formation (ΔH_f)
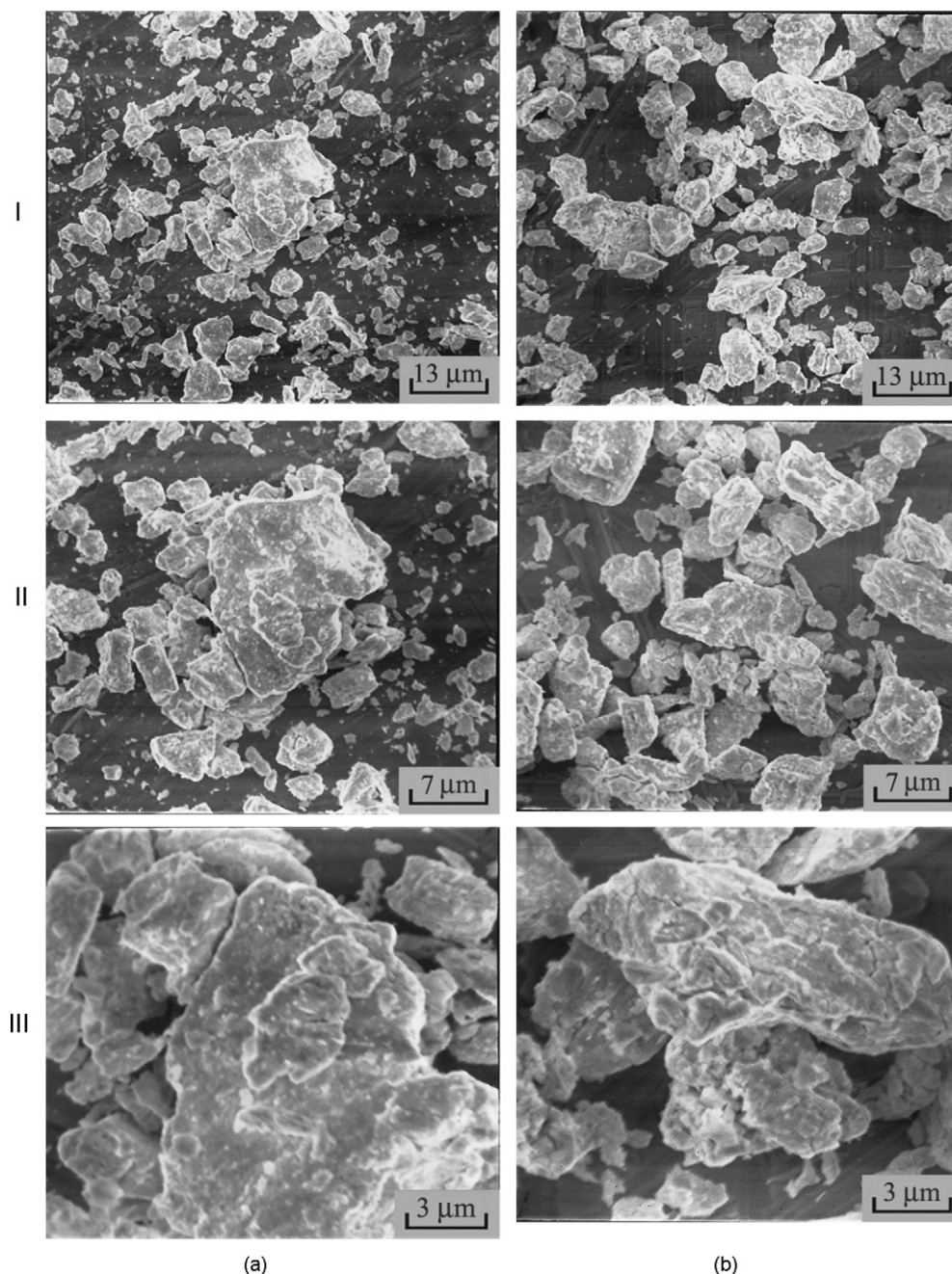

Fig. 5. SEM images of Hf$_2$Ni: (a) before absorption and (b) after 20 cycles of absorption/desorption processes at 673 K; amplifications: 600 (I), 1000 (II) and 2000 (III).

which implies greater intermetallic stability, Table 1. Also, all the investigated Hf-based intermetallics are good hydrogen absorbers with high values of hydriding capacity (Table 2). Amongst the investigated intermetallics, Hf_2Fe is the best absorber with the largest hydriding capacity and rate constant of the absorption process obtained at 573 K (Table 2), and the lowest value of activation energy (Table 1).

4. Conclusions

The investigated Hf-based intermetallics are better cathode materials in the HER reaction than the commercial cathodes Ni and Fe. From the obtained experimental results it is obvious that the investigated Hf-based intermetallics are good hydrogen absorbers and could be ordered according to their absorption abilities, both absorption kinetics and hydriding capacities, as follows: $Hf_2Fe > Hf_2Co > Hf_2Ni$.

Acknowledgement

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