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Design of Zr-based AB_2 type hydrogen storage alloys①

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Abstract: The influences of the ratio of the radius of atom A(r_A) to radius of atom B(r_B), electronegativity and electron number were discussed on the Laves phase formation and the characteristics of Zr-based AB_2 type hydrogen storage alloy. An enthalpy model of Zr-based AB_2 alloy was obtained from known data and twelve Zr-based alloys were designed to test the model. The results show that the predicted values are in good agreement with the experimental values. The model can be used for predicting enthalpy values of Zr-based hydrogen storage alloys and settles a foundation for experiments.

Key words: Zr-based AB_2 type hydrogen storage alloy; enthalpy model; design
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1 INTRODUCTION

Presently, there are two kinds of hydrogen storage alloys (AB_5 and AB_2) used in nickel-metal hydride (Ni/MH) battery. AB_2 type hydrogen storage alloy has worse activation performance and lower initial capacity though its capacity is higher and life is longer than AB_5 alloy. At the same time, AB_2 type hydrogen storage alloy is more expensive than AB_5 type hydrogen storage alloy. All the above aspects embarrass the actual application of AB_2 type hydrogen storage alloy. Properties of AB_2 type hydrogen storage alloy, such as capacity, activation, and circle life, are closely related with the component and structure of the alloy. So it is necessary to study on the component and structure of the alloy in order to optimize the design of the alloy, to improve the activation performance of Zr-based hydrogen storage materials, to reduce the cost and to accelerate the application of AB_2 type hydrogen storage alloy.

2 DESIGN OF ALLOY

Zr can form AB_2, AB_{2+a} Laves phase hydrogen storage alloys with metals such as V, Mn, Cr and so on. B atom can be partially replaced by Ni, Co, Fe and so on. Laves C15 and C14 phase can store hydrogen and C15 structure has the most hydrogen storage capacity[1]. The effects of all kinds of factors on alloy preparation are discussed below.

2.1 Laves phase formation conditions

The radius of atom A(r_A) must be larger than that of atom B(r_B). The ideal formation is r_A: r_B= 1.225 . If r_A: r_B> 1.24, single C15 Laves phase formed. It is apt to form C14 Laves phase when the ratio of r_A to r_B is lower than 1.24[2]. Another factor is average number (n) of outside electrons. When n= 4.67－5.4, C15 Laves phase formed in the Zr-based alloys. When n= 5.4－7.0, C14 Laves phase formed in Zr-based and Ti-based alloys. When n> 7.0, C15 Laves phase formed. Besides, the crystal structures of alloys have great relation to the average concentration of electron[3]. When the electron concentration (e/a) is greater than 2.3, C15 Laves structure is apt to form.

2.2 Effects of elements replacement

According to atom radium, replacement of one main element in a alloy with a larger radium element results in a larger absolute value of $\Delta H^{\ominus}$, which means that the hydride between metals is more stable. The absolute value of $\Delta H^{\ominus}$ is also related with chemical appetency between elements. When one element in a alloy is replacement by a more electronegative element, the average electronegativity in the alloy become larger and absolute value of $\Delta H^{\ominus}$ decreases, which means that the hydride between metals becomes more unstable.

$\Delta H^{\ominus}$ is related with not only the kind of replaced element, but also the quantity of replaced element.

$$r_{av}= \sum a_i r_i / \sum a_i = (r_A + 2r_B)/3 \quad (1)$$

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where r_{av} is mean atom radium, a_i is the number of atom i. Decrease of r_{av} reduces the volume of crystal lattice and the absolute value of $\Delta H^{\ominus}$ of hydride formed in the alloy.

$$x_{av} = \sum a_i x_i / \sum a_i \quad (2)$$

where x_{av} is mean electronegativity.

When x_{av} increases, the affinity between hydrogen and alloy becomes smaller and the absolute value of $\Delta H^{\ominus}$ decreases.

2.3 Effects of elements

Ti and Zr can not only store hydrogen as fundamental elements in alloy, but also form thick, inactive oxide in basic solution. V can form dissolvable oxide. Cr can prevent V from excessive corrosion and control the microstructure of alloy. Zr is in favor of controlling brittle and increases the surface area of electrode, however it accelerates the electrode reaction. Too fragile electrode mechanically decomposes easily, and as a result conductivity is lowered and polarization increased. So the circle life of cell is shortened. Sufficient attention should be paid to this point.

Ni has several important effects in alloy. Firstly, linking power between alloy powders for cathode and hydrogen should be suitable. When there is Ni in alloy, linking power between Ni and H is strong and linking power between V, Ti, Zr and H is infirm, so the linking power between alloy and H can be adjusted by controlling the content of Ni, and also that of V, Ti, Zr. Secondly, Ni is a catalyst for hydrogen decomposition and accelerates the gas-solid reacting velocity. Finally, Ni has the characteristics of anti-oxidation and anti-corrosion. Alloy made of Ni, V, Ti and Zr has better anti-oxidation property, and forms a film of oxide at the interface of electrode and electrolyte solution. Because the film contains metal Ni, this is resulted in the increase of conductivity and catalytic activity of the alloys.

3 THERMODYNAMIC COMPUTING MODEL OF HYDROGEN STORAGE ALLOYS

The results above show that the thermodynamic characteristics of hydrides play an important role on the performance of hydrogen storage alloys. Research on the disciplines is helpful to developing hydrogen storage alloys. We can deduce whether one alloy is useful for hydrogen storage according to its thermodynamic characteristics.

Relation between forming enthalpy of Zr-based alloy hydrides and atom bond parameters is analyzed and a model is presented.

In general, the energies of alloys involve three factors:

1) Chemical affinity represented by electro-negativity;

2) Atom size;

3) Electron concentration.

According to the bond parameters above, enthalpy change (ΔH) of alloy formatting hydride can be expressed as below[4]:

$$\Delta H = a_0 + a_1(\Delta x)^2 + a_2\delta^2 + a_3\left(\frac{e}{a}\right)^{\frac{2}{3}} \quad (3)$$

where a_0, a_1, a_2, a_3 are constants, Δx is electronegative difference of multi-element alloys, δ is atom size factor, e/a is electron concentration factor.

Collecting 12 groups of data and computing with step reduce analyzing method on a computer and the result is shown as below[5-11]:

$$\Delta H = -8.813\times10^4 + 3.56\times10^5(\Delta x)^2 - 1.879\times10^6\delta^2 + 1.995\times10^4\left(\frac{e}{a}\right)^{\frac{2}{3}} \quad (4)$$

The relative factor R is 0.944.

Enthalpy change ΔH_{cal} calculated with Eqn. (4) and ΔH_{exp} from Ref. [5-11] all locate on the sides of 45 degree line (as shown in Fig. 1), which means that the experimental results are in good agreement with the predictedones. The model is tested with the 12 hydrogen storage alloys designed in this paper (AB_2-0, AB_2-1, ···AB_2-11), and the results show that $-\Delta H_{exp}$ and $-\Delta H_{cal}$ have near values (as listed in Table 1), which means that the model presented in this paper is reasonable. Enthalpy change of AB_2 type hydrogen storage alloys can be predicted with this model and a foundation of theory for the design and development of hydrogen storage alloys.

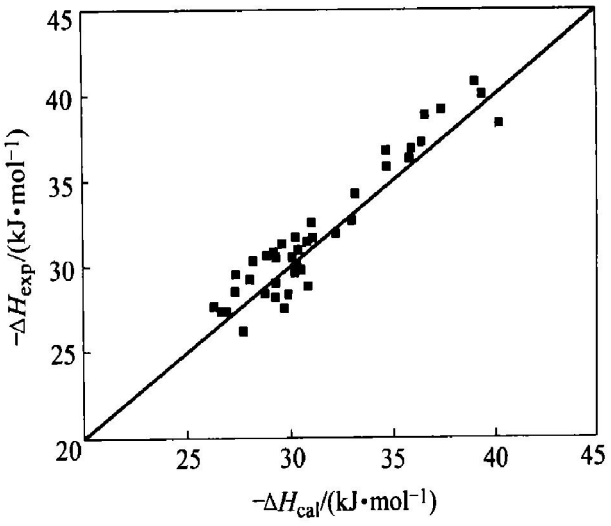

Fig. 1 Comparison between calculated and experimental ΔH for hydrogen storage alloy

Table 1 Enthalpy of hydrogen storage alloy

Alloy	$-\Delta H$ / (kJ·mol^{-1})	
	Experimental	Calculated
AB_2-0	30.64	32.03[11]
AB_2-1	34.03	33.15[11]
AB_2-2	–	29.20
AB_2-3	–	26.12
AB_2-4	35.78	34.89[11]
AB_2-5	34.01	35.82[11]
AB_2-6	–	43.34
AB_2-7	45.52	45.38[11]
AB_2-8	38.69	39.41[11]
AB_2-9	30.69	31.50[11]
AB_2-10	–	31.12
AB_2-11	–	29.49

4 CONCLUSIONS

1) The ratio of r_A to r_B, electronegativity, outer electrons number and effects of elements play important roles on the property of the Zr based AB_2 type hydrogen storage alloy, such as temperature characteristic, activity, high rate discharge, cycle life and so on. A thermal model for the enthalpy change of the alloy, ΔH is obtained and is testified with 12 Zr-based hydrogen storage alloys.

2) The predicted values are in good agreement with the experimental values. The model can be used for predicting enthalpy values of Zr-based hydrogen storage alloys and settles a foundation for experiments.

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