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Effect of porosity on hydrogenation kinetics of $Mg\text{-}3Ni\text{-}2MnO_2$ nanocomposite powder reaction bed

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Abstract: Hydrided $Mg\text{-}3Ni\text{-}2MnO_2$ composite powders were fabricated by reactive ball milling with hydrogen, and accumulative hydrogenation kinetics and temperature field of reaction bed with various porosities (0.37, 0.53 and 0.63) were measured. The results show that the accumulative hydrogenation kinetics of $Mg\text{-}3Ni\text{-}2MnO_2$ powder reaction bed depends strongly on the effect of heat transfer, mass transfer and intrinsic reaction together. The reaction bed with the porosity of 0.53 exhibits the largest hydrogenation rate. During the hydrogenation process, the temperature of reaction bed rises quickly due to the fast release of heat, and the temperature difference between center and wall with 0.53 porosity can keep high even for a long time, which promotes fast heat transfer. The further analysis indicates that more emphases should be put on heat transfer rate rather than the only improvement of the effective thermal conductivity.

Key words: hydrogen storage materials; porosity; heat transfer rate; reaction bed

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1 Introduction

Mg-based hydrogen storage material is considered a privileged material owing to its high hydrogen storage capacity (the theoretical capacity of MgH_2 is 7.6%)[1]. In recent years, some Mg-based hydrogen storage composites with fast intrinsic hydrogenation and dehydrogenation dynamics have been developed[2−3]. The hydrogen storage materials can be used widely in industries[4−5]. However, it is evident that the poor thermal conductivity and mass transfer of reaction bed probably become the obstacles for their further application[6]. Therefore, the study of heat and mass transfer is desired in a metal-hydrogen reactor during hydrogenation and dehydrogenation process[7−9].

Up to present, although some studies on the reaction bed of Mg-based hydrogen storage materials have been carried out, most of them are focused on the numerical simulation[10−11]. The $Mg\text{-}3Ni\text{-}2MnO_2$ hydrogen storage material, developed by our group, has shown excellent intrinsic hydrogenation kinetics[12], hence the study about the effect of porosity on the accumulative hydrogenation kinetics of reaction bed is a key issue for its industrial application.

2 Experimental

In this work, the starting materials, preparation method of composite powders and measuring apparatus were the same as those in Ref.[13], then the $Mg\text{-}3Ni\text{-}2MnO_2$ hydrogen storage materials were fabricated. The schematic diagram of reaction bed configuration and the distribution of thermocouple is shown in Fig.1, and the geometry size of reaction bed is listed in Table 1. In order to evaluate the experimental result reasonably, the phase transformation fraction of reaction bed during hydrogenation is plotted as a function of time. The phase transformation fraction is defined as the ratio of actual hydrogen capacity(H/M) to theoretic capacity (7.6%). The averaged porosity, ε, can be calculated by

$$\varepsilon=\frac{V_m-V_s}{V_m} \tag{1}$$

where V_m is actual volume of powder bed, and V_s is the volume sum of Mg; Ni and MnO_2 are considered to be solids.

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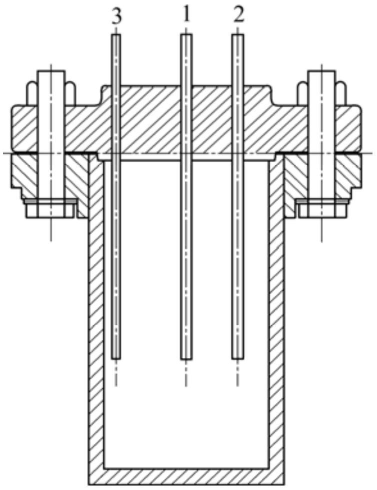

Fig.1 Configuration of reaction bed and distribution of thermocouples: 1—r=0 mm; 2—r=6.25 mm; 3—r=12.5 mm

Table 1 Geometry size of reaction bed

Length of cylinder/mm	Inner radius of inner cylinder/mm	Thickness of cylinder wall/mm
120	12.5	3.5

3 Results and discussion

3.1 Hydrogenation kinetics in powder reaction bed

The hydrogenation process of reaction bed was performed under the initial temperature of 200 ℃ and hydrogen pressure of 2.0 MPa. Fig.2 shows the hydrogenation phase transformation fractions of the Mg-3Ni-2MnO$_2$ powder reaction bed as the function of time, which includes three curves corresponding to the porosities of 0.37, 0.53 and 0.63. From Fig.2, the reaction beds with different porosities all exhibit rapid hydrogenation rates at the initial stage, and this characteristic is mainly related to its fast intrinsic reaction rate[12]. With the reaction proceeding, the hydrogenation rates of all the reaction beds slow down after the reaction fraction reaches about 0.5, which results from different reaction rates of local position in reaction bed. The different porosities lead to the variation of accumulative hydrogenation kinetics and the bed with porosity of 0.53 exhibits the relatively faster reaction rate than the other two cases.

The reason why the accumulative hydrogenation kinetics is so different from its intrinsic hydrogenation kinetics is mainly the effect of transient heat transfer, mass transfer and intrinsic rate together, and at the same time, coupling effect from the heat transfer, mass transfer and intrinsic rate always occurs. Fig.3 shows hydrogenation kinetics and temperature variation of Mg-3Ni-2MnO$_2$ hydrogen storage materials of 1 g under 2.0 MPa hydrogen pressure. In this situation without consideration of mass transfer, it takes several seconds for this hydrogen storage material to complete hydrogenation process due to the strong coupling between hydrogenation reaction and release of heat. Hence, it is difficult to discuss the effect of each factor on the accumulative hydrogenation kinetics.

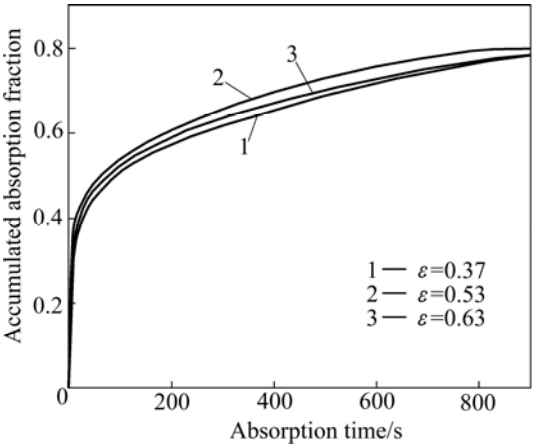

Fig.2 Effect of porosity on accumulated hydrogenation kinetics of Mg-3Ni-2MnO$_2$ reaction bed

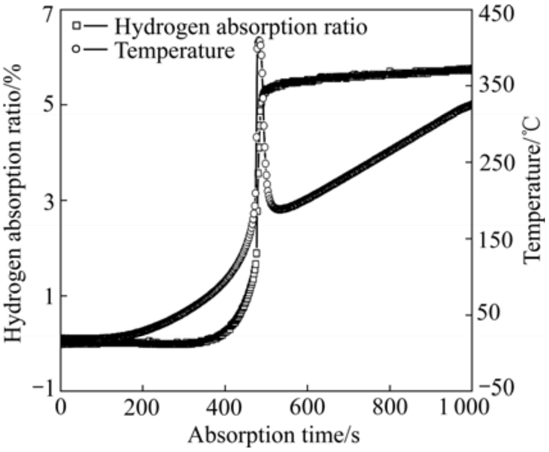

Fig.3 Hydrogenation kinetics and temperature variation profiles of Mg-3Ni-2MnO$_2$ of 1 g under 2.0 MPa hydrogen pressure

Through acting on the heat and mass transfer process, the porosity affects strongly the accumulative hydrogenation kinetics. The temperature of reaction bed can be measured macroscopically. In order to attain reasonable conclusions about the accumulative hydrogenation kinetics, the influence of temperature field in reaction bed must be analyzed.

3.2 Temperature field revolution of reaction bed

Fig.4 illustrates the temporal and spatial variation of temperature field of this powder reaction bed during hydrogenation process, including three figures corresponding to the porosities of 0.37, 0.53 and 0.63. From Fig.4, the initial temperature of different fields in the reaction bed increases sharply. It is well known that

$Mg-H_2$ reaction is exothermic and the heat of 74.4 kJ/mol(H_2) is released. When the heat transfer rate is lower than that of the heat release, much heat is transferred out of bed and the other heat is used to heat the reaction bed. Work of Ref.[12] shows that the intrinsic hydrogenation rate of $Mg-3Ni-2MnO_2$ powders is so fast that massive heat is released at the same time, and the excessive heat is stored in the hydride bed to cause a rapid rise of temperature of the bed. According to Fig.4, the temperature of different positions in reaction bed is higher than the initial temperature of 200 ℃.

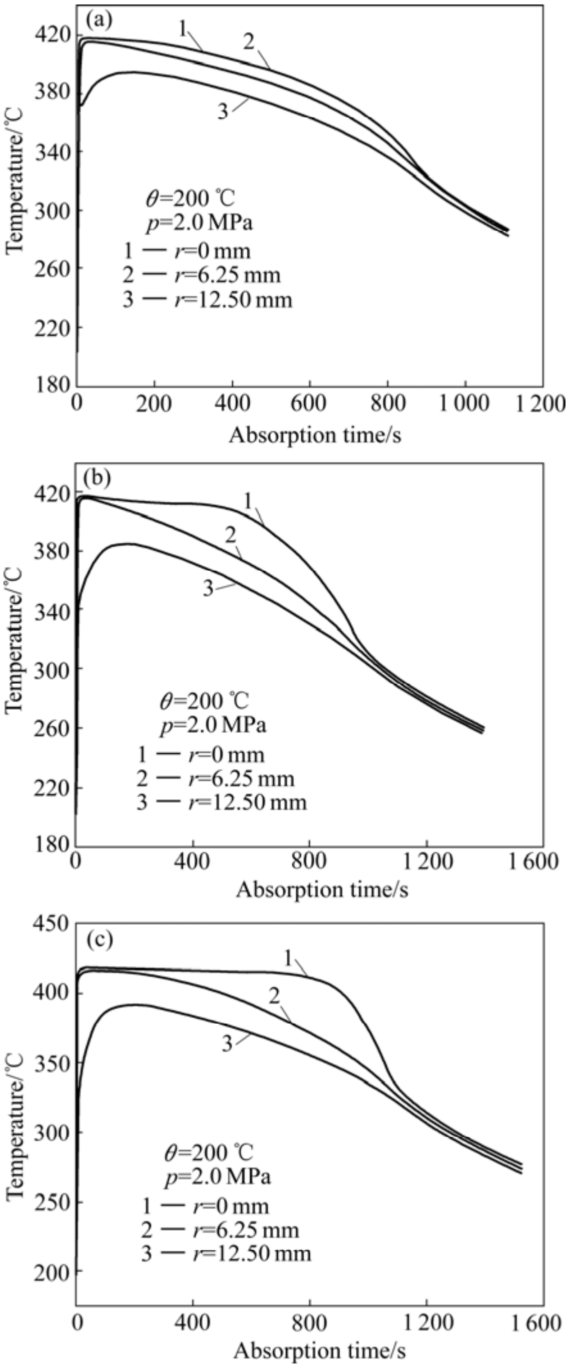

Fig.4 Temperature field evolution of $Mg-3Ni-2MnO_2$ reaction bed with different porosities during hydrogenation process: (a) $\varepsilon=0.37$; (b) $\varepsilon=0.53$; (c) $\varepsilon=0.63$

The local temperature of reaction bed is different from each other after hydrogenation, and the temperature of central location can achieve the maximum of 420 ℃, much higher than that close to wall, resulting from the good heat exchange between the inside and outside of the bed. The temperature of the bed decreases continuously from center to convective wall in radial direction. The maximum temperature of about 420 ℃ is only related to the inlet pressure of bed and the porosity has no obvious effect on it. Usually, the equilibrium pressure of $Mg-H_2$ reaction rises with the increasing temperature. Fig.5 shows plateau pressure profiles of $Mg-3Ni-2MnO_2$ hydrogen storage material as a function of temperature. The sharp increase of the local temperature in the hydride bed could reduce the pressure difference between inlet pressure and equilibrium pressure ($p_{\text{inlet}}-p_{\text{eq}}$) and the intrinsic reaction rate starts to decline. Even the local hydrogenation rate is decreased to zero when the hydriding equilibrium pressure becomes equal to the inlet pressure. At the same time, the heat release will be stopped immediately. Only when much heat is transferred out of this location and mass transfer of hydrogen is fast enough to keep the location pressure at 2 MPa, this local temperature will keep dynamically stable. This conclusion can be verified by the Figs.4(b) and (c). According to Darcy law[14], the less the porosity is, the lower the permeability is, hence, the mass transfer rate of bed with 0.37 porosity is so low that local pressure cannot be kept at 2 MPa, as a result, local temperature declines gradually, as shown in Fig.3(a). The temperature field revolution also results from the interaction of heat transfer, mass transfer and intrinsic reaction.

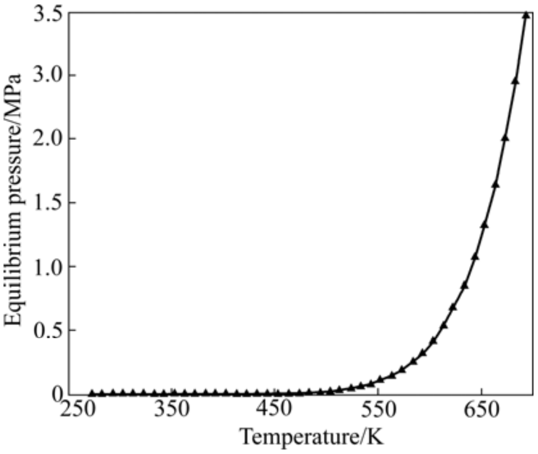

Fig.5 Plateau pressure profile of $Mg-3Ni-2MnO_2$ hydrogen storage material as function of temperature

With reaction proceeding, the temperature close to the wall starts to decline gradually after a maximum temperature; and the temperature revolution of $r=6.25$ mm location with various porosities is different from each another. The general characteristic is that the time of the central temperature can keep much long with porosity rising. Similarly, the larger the porosity is, the longer the keeping time of uniform temperature field for reaction bed temperature will be.

3.3 Interaction between hydrogenation reaction and heat transfer

It is well known that the hydrogenation process of reaction bed is a transient heat transfer, mass transfer and intrinsic one, and the two parameters of accumulative hydrogen capacity and temperature can be measured macroscopically just in time, whose real values are resulted from the interaction of heat transfer, mass transfer and intrinsic process. To further investigate the effect of porosity on the accumulative hydrogenation kinetics, the whole reaction bed is chosen as an objective to be studied.

The overall heat transfer of reaction bed consists of the effective thermal conductivity of bed and conductivity of bed wall, and the effect of bed wall conductivity and heat exchange between cooling fluid and bed on the hydrogenation can be indicated by the average bed temperature revolution. The main heat transfer can be considered to proceed in the radius direction rather than in axial direction due to the large ratio of length to radius. Furthermore, Fourier heat transfer equation is referenced to analyze the effect of heat transfer rate on the hydrogenation kinetics:

$$q=\frac{\lambda}{\delta}(\theta_{\mathrm{w}1}-\theta_{\mathrm{w}2}) \tag{2}$$

where q is the heat flux (W/m^2); λ is the effective thermal conductivity (W/(m·℃)); δ is the distance (m); ($\theta_{\mathrm{w}1}-\theta_{\mathrm{w}2}$) is the temperature difference (℃).

In Ref.[15], the static-method has ever been employed to measure and calculate the effective thermal conductivity of hydrided Mg-3Ni-2MnO$_2$ powder reaction bed. Although there should be difference between static value and real value, the trend of value variation is still effective qualitatively. The general characteristic is that the effective thermal conductivity is very poor (＜2 W/(m·K)) and rises with porosity decreasing.

Fig.6 reveals the profiles of temperature difference between center and wall as a function of time. For the most time of process, the reaction bed with the porosity of 0.53 has the highest value of ($\theta_{\mathrm{w}1}-\theta_{\mathrm{w}2}$) while the reaction bed with the porosity of 0.37 has the lowest one. When considering δ to be constant and the order of magnitude of λ being less than that of temperature difference, the highest value of ($\theta_{\mathrm{w}1}-\theta_{\mathrm{w}2}$) leads to the largest of q according to Fourier heat transfer equation, and the bed with 0.53 porosity possesses the largest heat flux. By combination with above results that the bed with 0.53 porosity exhibits excellent accumulative hydrogenation kinetics, it is concluded that rising heat transfer rate will promote the hydrogenation reaction. In other words, more emphases should be put on transient heat transfer rate rather than the only improvement of the effective thermal conductivity in the reaction bed design of Mg-3Ni-MnO$_2$ hydrogen storage materials.

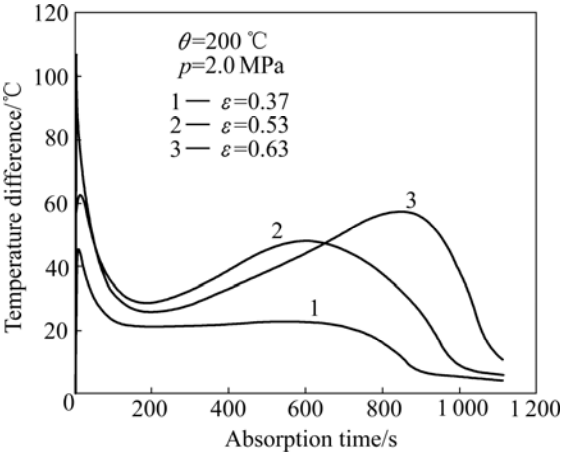

Fig.6 Temperature difference profiles between center and wall of reaction bed during hydrogenation

4 Conclusions

1) The transient hydrogen capacity and temperature of Mg-3Ni-MnO$_2$ hydrogen storage material reaction bed are affected by the co-effect of heat transfer, mass transfer and intrinsic reaction. Through affecting on the heat and mass transfer process, the porosity influences strongly on the accumulative hydrogenation kinetics.

2) During hydrogenation process, the temperature of the reaction bed rises sharply at initial stage due to exothermic reaction. The temperature difference between center and wall of reaction bed with 0.53 porosity keeps the highest, promoting the hydrogenation process.

3) The further analysis indicates that more emphases should be put on heat transfer rate rather than the only improvement of the effective thermal conductivity in reaction bed optimal design.

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