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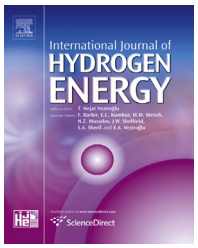

Study on preparation and properties evaluation of Mg/Ni/Ti hydrogen storage material

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ABSTRACT

The improvement of the capacity and rate of hydrogen absorption/desorption at the same time had been focus hydrogen storage field. A new method was proposed to prepare a new type sintered body with a special layer structure due to the crystal structure of the sintered body distinguish with a powder and alloy. Therefore, the sintered body not only effectively overcame the inconvenience from the powder on storage aspect, but also avoided negative factors of small surface area. The sintered body had a foam structure whose surface area was large, which provided a strong chemical channel for the physical absorption and chemical diffusion by generating hydrogen absorption phase Mg_2Ni and catalytic phase NiTi, so that great improved the property of hydrogen absorption/desorption. The capacity of hydrogen absorption/desorption reach to 3% within 3 min and the highest capacity reach to 5.26% within 16 min; hydrogen desorption process was completed within 30 min and the released capacity was about 2%.

Introduction

Hydrogen is very promising energy source as a new clean energy. However, the safe storage of hydrogen is very difficult because of its explosive nature [1,2]. Therefore, hydrogen storage materials as carrier has been investigated and developed. Among the many metal hydrides, magnesium hydride is most potential because of its high storage capacity (7.6 wt. %), low density and low cost [3–6]. In the past few years, Mg-based hydrogen storage material, which had been used widely as aviation, communications and electronics fields. However, its high hydrogen desorption temperature, high activation energy restrict the use of Mg in wide and spread practical applications [7–9]. Recently, Mg_2Ni showed significant gravimetric hydrogen capacity by specific milling conditions and proper composition, but still existed disadvantages that the powder is easy to chalk and not easy to store; the rate of hydrogen absorption/desorption was slowly [10,11]. To reduce the negative factors in absorbing and desorbing hydrogen, many researchers from home and abroad have conducted a large number of experiments to improve kinetic and thermodynamic properties [12,13]. In recent years, a superlattice structure Mg–Ni-based multiphase hydrogen

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storage alloy had obtained great attention because their activation performance was higher. The disadvantages that the temperature of hydrogen absorption and desorption was high and difficult to active had been pay close attention. So it is urgent to develop some new-type materials with higher activation capacity and lower cost in order to enhance the competition ability and to replace expensive materials [14]. Yet, the gravimetric capacity is not expected to rise significantly because the intrinsic capacity is not much higher. It is known that Mg/Ni/Ti based alloys with high dynamic performance and excellent activation have been considered as new candidates for hydrogen storage applications. But the study about the effects of such factors as temperature and H_2 pressure on hydrogen absorption and desorption is not sufficient [15]. The study with a new laminated cover method by changing element was conducted and was discussed to prepare the sintered body of the special structure. Its large surface area can effectively ensure the effective cycle of hydrogen absorption/desorption, so the whole cycle was completed within a very short time. In the process, the capacity of hydrogen absorption/desorption was obviously improved. The shortcoming of a powder inconvenient for storage and distribution was avoided and that of an alloy hard to activate was improved. The sintered body prepared in this experiment had uniform crystal structure and transitional layer which promoted hydrogen absorption/desorption. The different diffused layers were composed based on the same size pure Mg ingot as substance; the different transitional layers were connected between each diffused layers and had the good continuity, which improved the property of hydrogen absorption/desorption.

Experimental

Ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$ (1.4 mol/L) and nickel chloride $NiCl_2 \cdot 6H_2O$ (1.4 mol/L) were used as starting materials by co-precipitation. The solute of the aqueous solution was completely dissolved at 50 °C; aqueous solution mixed was stirred at the rate of 300 rpm for 2 h. Aqueous solution stirred was filtered with the funnel and filter paper. The mixed powder was sintered at 10 °C/min to 700 °C by using electric furnace. After sintering powder Ni was formed. In the secondary sintering process, Ti was added into powder Ni powder cover on pure Mg ingot under the molar ratio of Ni: Ti: Mg = β: γ: η and was sintered at 10 °C/min under the room temperature to 750 °C by electric furnace. As shown in Fig. 1, the special laminated cover method was used to form the sintered body, in which a large surface area generated in each layer. Alloy phases Mg_2Ni and NiTi were mainly formed on the surface and in the internal of the sintered body. The experimental purpose that generating absorbing hydrogen phase and catalytic phase was achieved by the new sintering method.

Characterizations

Crystalline phase structure was characterized by high temperature X-ray diffraction (XRD) with Cu-Kα radiation, scanned in the 2θ range of 30–80° at different temperature. The morphology and microstructure of the sintered body were observed by using a JEM-2100F transmission electron microscopy (TEM). Sievert type pressure-composition-temperature (PCT) volumetric apparatus was used to evaluate the capacity of hydrogen absorption and desorption under different hydrogen pressure and temperature. Hydrogen absorption and desorption curves at various conditions were obtained to confirm the absorbing and desorbing properties of the sintered body.

Results and discussion

Growth of crystal grains

Pure Mg ingot was covered with the Ni Powder and Ti powder at the molar ratio of Ni: Ti: Mg = β: γ: η after grinding for 2 h and then sintered at 10 °C/min at the room temperature to 1000 °C by high temperature X-ray. Ti was added to refine crystal grains by forming new alloy phase; the purpose of this experiment is to buffer the deformation from large Mg crystal grains by new phases. Mg ingot played an importance role as a substance and made diffused powder on which achieve uniform and refined. The process was calculated and analyzed with gradually heating temperature. The mixed powder Ni and Ti powder contacted directly with pure Mg ingot, so that leaded to generation of the Mg_2Ni and NiTi alloy phases. It is

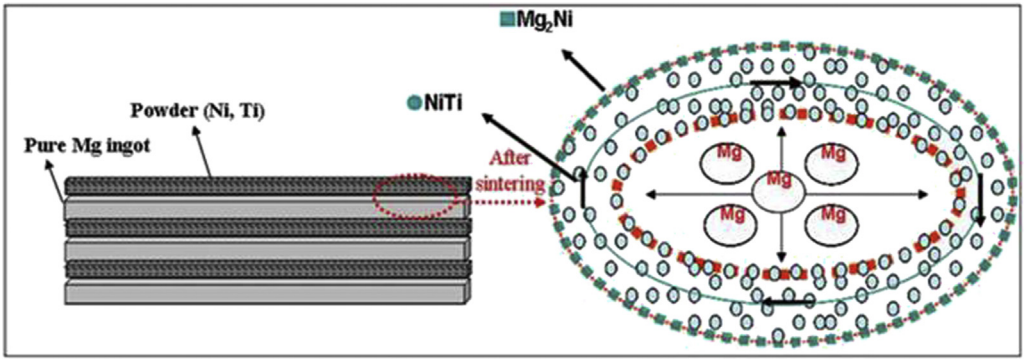

Fig. 1 – Mechanism of forming alloy phase.