



High activity retention Al–Bi–Zn-base composite powder with mild hydrogen generation

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Abstract: Al–10Bi–7Zn and Al–10Bi–7Zn–1.5X (X: Cu, Fe, Ni, in wt.%) composite powders were designed and prepared through phase diagram calculation and gas atomization method. The effects of Cu, Fe, and Ni on the hydrolysis of Al–Bi–Zn-base composite powders for hydrogen production were investigated respectively. The composition and morphology of powders were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy disperse spectroscopy (EDS) analyses. Hydrolysis performance test results indicate that the additions of Cu, Fe, or Ni can modify the hydrogen production rate and enhance oxidation resistance in Al–10Bi–7Zn ternary alloy composite powder. In the quaternary composite powder system, Al–10Bi–7Zn–1.5Ni (wt.%) exhibits the best performance with the hydrogen generation yield of 75.3% (954.1 mL/g) within 500 min when reacting with distilled water at 60 °C and maintains a hydrogen yield of 57.9% (733.7 mL/g) within 1500 min after being stored (30 °C, relative humidity of 60%) for 7 d. In addition, the mechanism investigation suggested that the additions of Cu, Fe, or Ni in Al–Bi–Zn-base composite powders can stabilize the Al matrix to retain the high activity of powders resulting from inhibiting the cracking of composite powders in the air.

Key words: aluminum alloy; gas atomization; hydrolysis reaction; hydrogen production; oxidation resistance

1 Introduction

With the development of society, people gradually realize that the massive use of fossil energy will bring about air pollution, greenhouse and other environmental problems [1]. Therefore, the search for renewable and clean energy has become an important subject for human beings. Among various new energies, hydrogen energy has the advantages of rich resources, clean, and high

energy storage density which is generally considered by researchers as one of the effective alternatives to traditional energy [2,3]. However, the application of hydrogen energy is still limited due to the difficulties in the production, storage and transportation of hydrogen [4]. Therefore, DENG et al [5] and HOLLADAY et al [6] put forward the concept of portable hydrogen production or on-board hydrogen production, which means that hydrogen production materials are directly used to produce hydrogen when hydrogen is on demand.

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Recently, on-board hydrogen generation via the hydrolysis of electrochemically active light metals such as Al [7] and Mg [8] has attracted much attention. In particular, Al is a very promising hydrolyzing material due to its low density, high efficiency and safety [9–11]. However, when Al reacts with water to generate hydrogen, a dense oxide film on the surface forms, hindering the contact reaction between Al and water, which leads to the reduction of the reaction activity [12]. The researchers found that putting Al in the alkaline or acidic solution can destroy the oxide film to produce hydrogen continuously [13–16]. However, both alkaline and acidic solutions will cause corrosion to hydrogen production equipment, which increases the cost and is harmful to the environment. In order to improve the reaction activity of Al in a neutral solution and maintain continuous hydrogen production by hydrolysis, researchers usually introduce additives such as salts [17], transition metal [18,19] and metal hydride [14] in Al by high-energy ball milling. The introduced additives can simulate the micro-galvanic cell effect with the Al matrix to improve the hydrogen production performance of the materials. Nevertheless, there are some defects, such as low hydrogen yield, high cost and harmful to the environment. Furthermore, some researchers found that reducing the activation energy of the Al–H₂O reaction is also a promising way to improve the hydrogen production capacity of Al-based materials [20]. However, there are still some defects, such as the cumbersome material preparation process. At present, adding low melting point metals to Al to obtain high hydrogen production efficiency is a widely used method [21]. TEKADE et al [22,23] utilized the volume diffusion of Ga inside the Al surface leading to the structural weakening of Al to activate waste aluminum for in situ hydrogen production successfully. QIAO et al [24] prepared Al alloy ingots with excellent hydrogen production performance through adding low melting point additives (Ga, Sn, In, etc.). However, Ga and In are extremely expensive and difficult to preserve at room temperature.

In recent years, WANG et al [25] prepared self-assembling Al–Bi–Sn ternary alloy powder by atomization method due to the stable and metastable liquid miscibility gaps in the Al–Bi system and Al–Sn. These powders have achieved an excellent hydrogen production capacity. However,

the use of Sn leads to a high hydrogen production cost, which causes difficulties in practical application. Furthermore, WANG et al [26] replaced Sn with Zn to obtain comparable hydrogen production performance while reducing the cost of hydrogen production, and (Al, Bi)–7Zn presented the best hydrogen production performance. Nevertheless, on the one hand, the hydrogen production rate of Al–Bi–Zn composite powder is too fast to use in a practical situation. The excessive hydrogen production rate requires greater demands on controlling hydrogen flow. Additionally, the hydrogen that cannot be consumed in time needs to be collected using a buffer, which increases the use cost and brings potential safety hazards. On the other hand, Al–Bi–Zn composite powder that is easily inactivated in the air requires highly sealed storage equipment. As the result, the practical application of Al–Bi–Zn composite powder is limited by hydrogen flow control and the high storage cost.

Therefore, it is necessary to find low-cost metal additives on the basis of the existing ternary system to obtain Al-based composite powder with a moderate hydrogen production rate and good oxidation resistance. As the previous research reported [27–29], adding a small amount of high melting point metal elements such as Cu, Fe, and Ni can effectively control the hydrogen production performance of powders. In this study, Al–10Bi–7Zn (wt.%) powder was designed by phase diagram calculation and prepared by the gas atomization method, and the composite powders of Al–10Bi–7Zn–1.5X (X: Cu, Fe, Ni, in wt.%) with the additions of Cu, Fe or Ni were designed and prepared based on phase diagram calculation to modify the rate of hydrogen production. The microstructures of the composite powders were observed. Their hydrogen production performances were studied at different temperatures. In addition, the antioxidant properties of the composite powders were also studied.

2 Experimental

In this study, Al–10Bi–7Zn and Al–10Bi–7Zn–1.5X (X: Cu, Fe, Ni, in wt.%, the same below) the same below composite powders were prepared by gas atomization method. The raw materials used in this study are bulk metals with high purity

(99.9%) Al, Bi, Zn, Cu, Fe, and Ni. The metal was melted in an arc melting furnace and then atomized with high-pressure argon (5–8 MPa). The alloy powder was collected in a powder collection tank with a butterfly valve and then placed in a glove box filled with argon. Finally, the powder was separately loaded into a marked glass bottle for subsequent research.

The hydrogen yield of composite powder was measured by the drainage method. The measuring device is shown in Fig. 1. A 100 mL flask reactor containing 0.3 g alloy composite powder is placed in a water bath. After the temperature (40, 50, and 60 °C) is stable, 10 mL of preheated distilled water is injected into the reactor (the temperature of preheated water is consistent with the reaction temperature). The hydrogen produced in the reaction bottle is dried through the drying tube and enters the gas collection bottle. The water pressure in the bottle flows out into the beaker placed on the balance. The actual hydrogen production is obtained by weighing the mass of water. According to the ideal gas equation, the calculation formula of hydrogen production conversion rate (α^{H_2}) is [26]

$$\alpha^{H_2} = \frac{y^{H_2}}{\left(\frac{w_{Al}m}{M_{Al}} \times \frac{3}{2} + \frac{w_{Zn}m}{M_{Zn}} \right) V} \times 100\% \quad (1)$$

where y^{H_2} is the actual hydrogen production; w_{Al} is the mass fraction of Al in composite powder; w_{Zn} is the mass fraction of Zn in composite powder; M_{Al} is the molar mass of Al; M_{Zn} is the molar mass of Zn; m is the mass of the reacted composite powder; V is the molar volume of the gas at the reaction temperature.

The morphology and microstructure of the powder were observed by scanning electron

microscope (SEM, SU-70, Hitachi, Tokyo, Japan). The elemental distribution and composition of composite powder were measured by energy disperse spectrometer (EDS) connected by SEM. The crystal structure of powder was determined by an X-ray diffraction (D8 Advance, Bruker, Madison, WI, USA). The powder was coldly inlaid with epoxy resin, followed by dry sandpaper and 0.25 μm polishing paste grinding and polishing to obtain the cross section of composite powder. In the anti-oxidation experiment, the samples were stored in a constant temperature and humidity chamber (30 °C, 60% relative humidity (RH)).

3 Results and discussion

3.1 Design of powder composition

Using the established thermodynamic database of Al-based alloys, the vertical section phase diagrams of Al-10Bi-(0-10)Zn, Al-10Bi-7Zn-(0-6)Cu, Al-10Bi-7Zn-(0-6)Fe, and Al-10Bi-7Zn-(0-6)Ni were calculated, respectively. As shown in Figs. 2(a-d), there is a stable miscibility gap in the liquid state in these systems, marked as the L_1+L_2 area in the diagrams. According to previous studies, the powder composition can be maintained in the liquid-phase miscibility gap regions by means of rapid cooling by gas atomization [30]. Therefore, alloy powders composed of Al-10Bi-7Zn, Al-10Bi-7Zn-1.5Cu, Al-10Bi-7Zn-1.5Fe, and Al-10Bi-7Zn-1.5Ni were designed and prepared. The calculated phase fractions during solidification in Al-10Bi-(0-10)Zn, Al-10Bi-7Zn-(0-6)Cu, Al-10Bi-7Zn-(0-6)Fe, and Al-10Bi-7Zn-(0-6)Ni are present in Figs. 2(e-h), which show that the stable liquid-phase miscibility gap appears with the decrease of temperature. Further, the Al_2Cu phase, Al_3Fe phase, and Al_3Ni phase appear in Al-10Bi-7Zn-1.5Cu, Al-10Bi-7Zn-1.5Fe, and Al-10Bi-7Zn-1.5Ni alloys, respectively.

3.2 Morphology and microstructure

Figure 3 shows the microstructures of Al-10Bi-7Zn, Al-10Bi-7Zn-1.5Cu, Al-10Bi-7Zn-1.5Fe, and Al-10Bi-7Zn-1.5Ni. As can be seen from Fig. 3(a), the Al-10Bi-7Zn alloy powder is good sphericity, in which the powder size ranges from 5 to 50 μm . The powder surface is composed

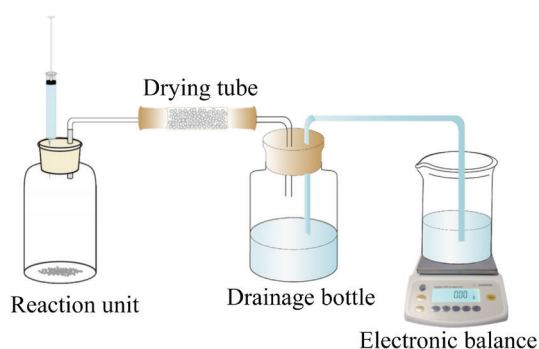


Fig. 1 Schematic diagram of experimental device used for hydrogen yield measurement

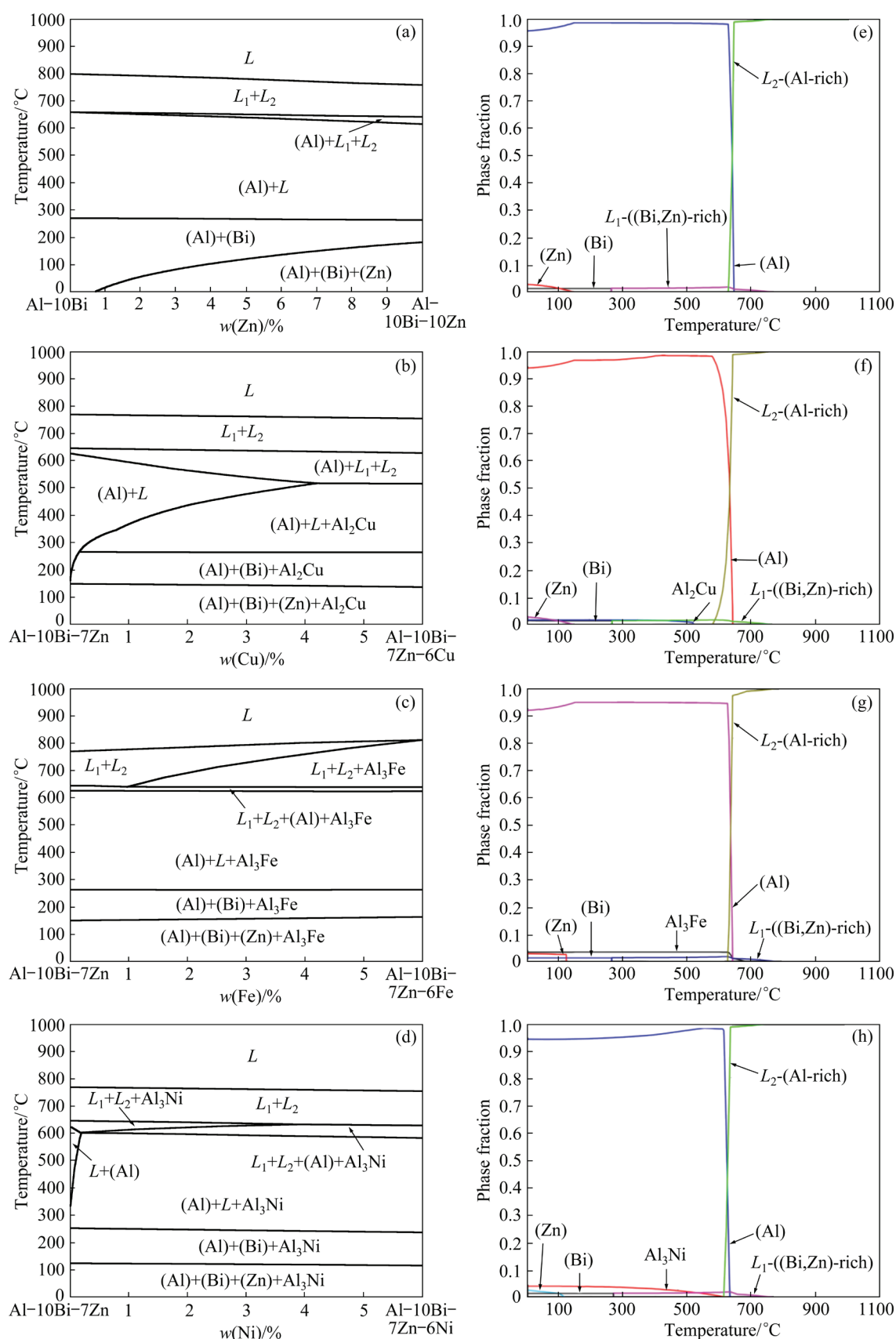


Fig. 2 Calculated vertical phase diagrams of Al–Bi–Zn, Al–Bi–Zn–X (Cu, Fe, Ni) (a–d) and calculated phase fractions (e–h) during solidification: (a) Al–10Bi–(0–10)Zn; (b) Al–10Bi–7Zn–(0–6)Cu; (c) Al–10Bi–7Zn–(0–6)Fe; (d) Al–10Bi–7Zn–(0–6)Ni; (e) Al–10Bi–7Zn; (f) Al–10Bi–7Zn–1.5Cu; (g) Al–10Bi–7Zn–1.5Fe; (h) Al–10Bi–7Zn–1.5Ni

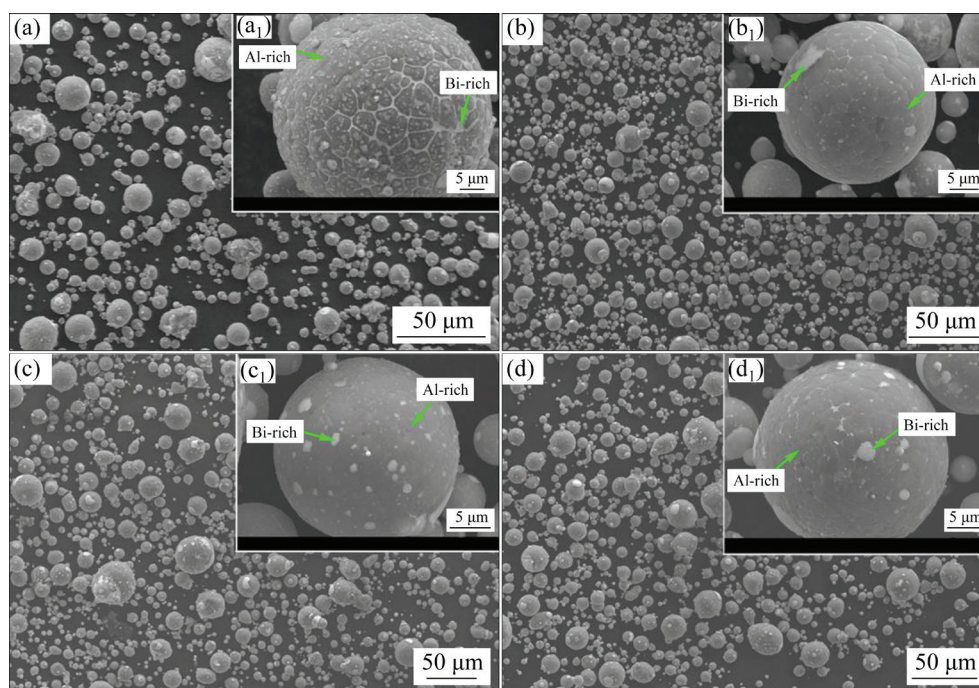


Fig. 3 SEM images of as-atomized Al-10Bi-7Zn and Al-10Bi-7Zn-1.5X composite powders: (a) Al-10Bi-7Zn; (b) Al-10Bi-7Zn-1.5Cu; (c) Al-10Bi-7Zn-1.5Fe; (d) Al-10Bi-7Zn-1.5Ni

of a white Bi-rich phase and a gray Al-rich phase. The Bi-rich phase mainly distributes continuously along the grain boundary, and a small part distributes separately within grain in the form of fine spots (Fig. 3(a₁)). After adding the fourth component, the powder size and sphericity did not change significantly, as shown in Figs. 3(b–d). In the meantime, it is worth noting that the addition of the fourth component will make the powder surface smoother. The continuous distribution of the white Bi-rich phase at the Al matrix grain boundary is reduced, and more Bi-rich phases distribute on the surface of the Al-rich phase in spots (Figs. 3(b₁–d₁)). The main reason maybe that the mixing enthalpy between elements is different [31]. Cu, Fe, and Ni elements will prefer to dissolve in the Al matrix and repel the Bi elements together. Bi elements will be more difficult to exist at the grain boundary of the Al matrix, so more Bi elements will be repelled to the surface of the Al matrix, and the spheres will look smoother. Figures 4(a–d) show the cross-sectional views of Al-10Bi-7Zn, Al-10Bi-7Zn-1.5Cu, Al-10Bi-7Zn-1.5Fe, and Al-10Bi-7Zn-1.5Ni composite powders. Inside the composite powder, the white Bi-rich phase dispersed at the grain boundary of the Al-rich phase. Figures 4(a₁–d₄) are the EDS mappings of Al-10Bi-7Zn and

Al-10Bi-7Zn-1.5X (X: Cu, Fe, Ni) powders. As displayed in the patterns, Zn, Cu, Fe and Ni are dissolved in the Al-rich phase matrix. The green spots in Figs. 4((a₂–d₂)) show the Bi-rich phase, which confirms that the white phase is the Bi-rich phase in Fig. 3.

Figure 5 shows the XRD patterns of the composite powders. The characteristic diffraction peaks of Al and Bi can be seen in the figure. The lack of characteristic peaks of Zn may be due to the large solid solubility of Zn in Al and the lack of precipitation under rapid cooling conditions [32]. In the meantime, from experimental phase diagrams of Ni–Al [33], Fe–Al [34], and Cu–Al [35] binary systems, it can be seen that there is a large solid solubility among Ni–Al, Fe–Al and Cu–Al. In particular, the cooling rate in the atomization process is very high, which inhibits the precipitation of the Al₃Ni phase, Al₂Cu phase and Al₃Fe phases [36–39].

3.3 Hydrogen generation performance

In this study, the effect of reaction temperature on the hydrolysis hydrogen production of quaternary alloy composite powder was studied. Figures 6(a–c) show hydrogen production per unit mass of Al-10Bi-7Zn-1.5Cu, Al-10Bi-7Zn-1.5Fe,

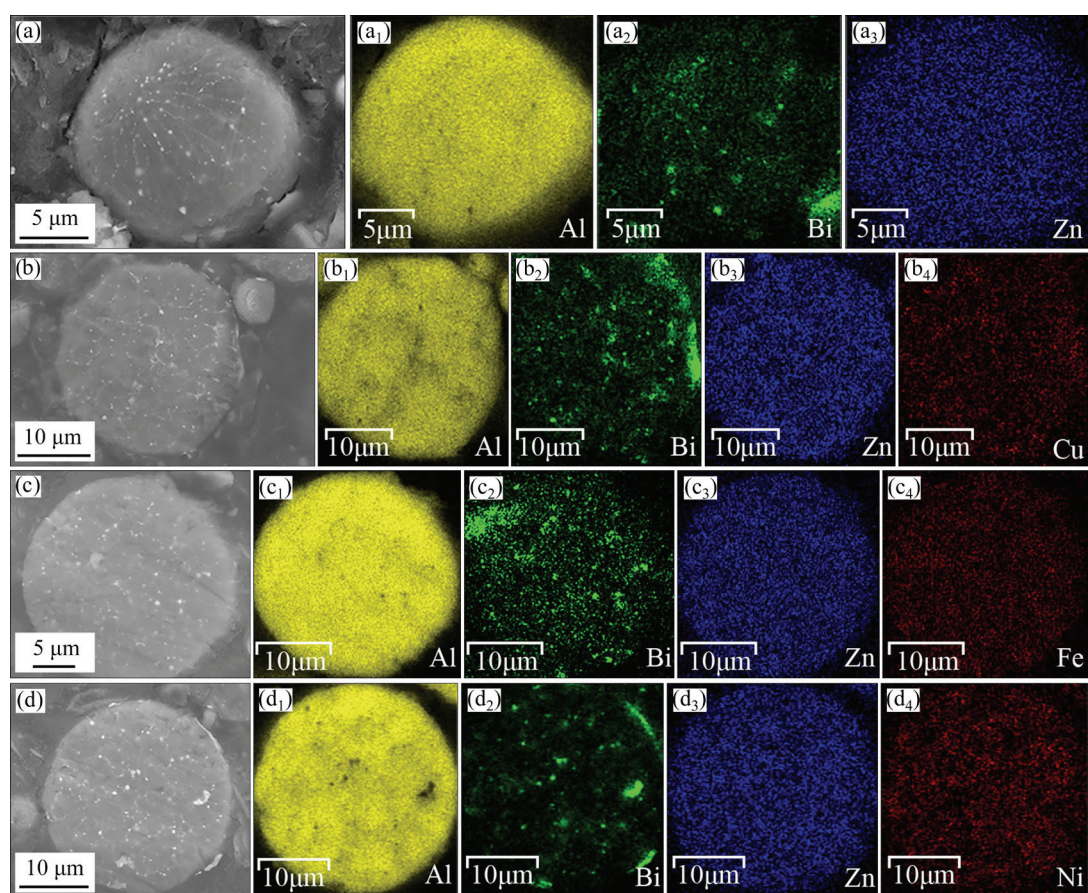


Fig. 4 SEM images and EDS mappings of cross-sections of Al-10Bi-7Zn and Al-10Bi-7Zn-1.5X composite powders: (a–a₃) Al-10Bi-7Zn; (b–b₄) Al-10Bi-7Zn-1.5Cu; (c–c₄) Al-10Bi-7Zn-1.5Fe; (d–d₄) Al-10Bi-7Zn-1.5Ni

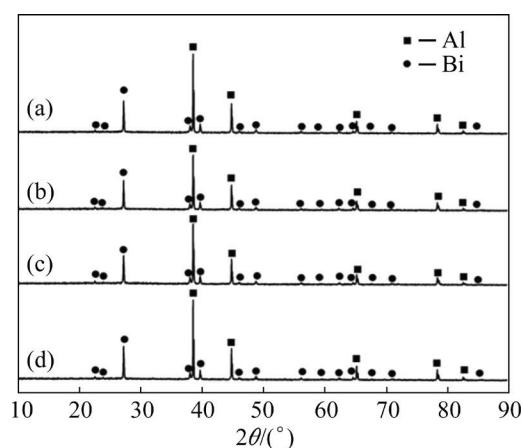


Fig. 5 XRD patterns of Al-10Bi-7Zn and Al-10Bi-7Zn-1.5X composite powders: (a) Al-10Bi-7Zn-1.5Ni; (b) Al-10Bi-7Zn-1.5Fe; (c) Al-10Bi-7Zn-1.5Cu; (d) Al-10Bi-7Zn

and Al-10Bi-7Zn-1.5Ni composite powders. These powders react with distilled water at different temperatures (40, 50 and 60 °C). Take an example, the hydrogen production curve of Al-10Bi-7Zn-1.5Cu composite powder at 40 °C can be roughly

divided into three parts. The initial stage is a dormant stage, which produces only a small amount of hydrogen for about 120 min and the yield is about 4.2% (50.0 mL/g). The next stage is the stage of constant growth, which is close to the stage of producing hydrogen at a constant rate. Hydrogen is produced at a constant rate within 150 min, and the yield is about 37.8% (450.2 mL/g). Then, the reaction enters the last stage of slow growth. The powder at this stage produces only a small amount of hydrogen until the end of the reaction. For Al-10Bi-7Zn-1.5Cu composite powder, the increase in temperature will make the reaction skip the dormancy period and change to only two stages, retaining the constant growth period and slow growth period. At the same time, the increase in temperature will improve the reaction activity of the powder, so as to greatly improve the hydrogen production per unit mass of the composite powder. When Al-10Bi-7Zn-1.5Cu composite powder reacts with distilled water at 60 °C, the hydrogen yield of 60.7% (769.0 mL/g) can be achieved in

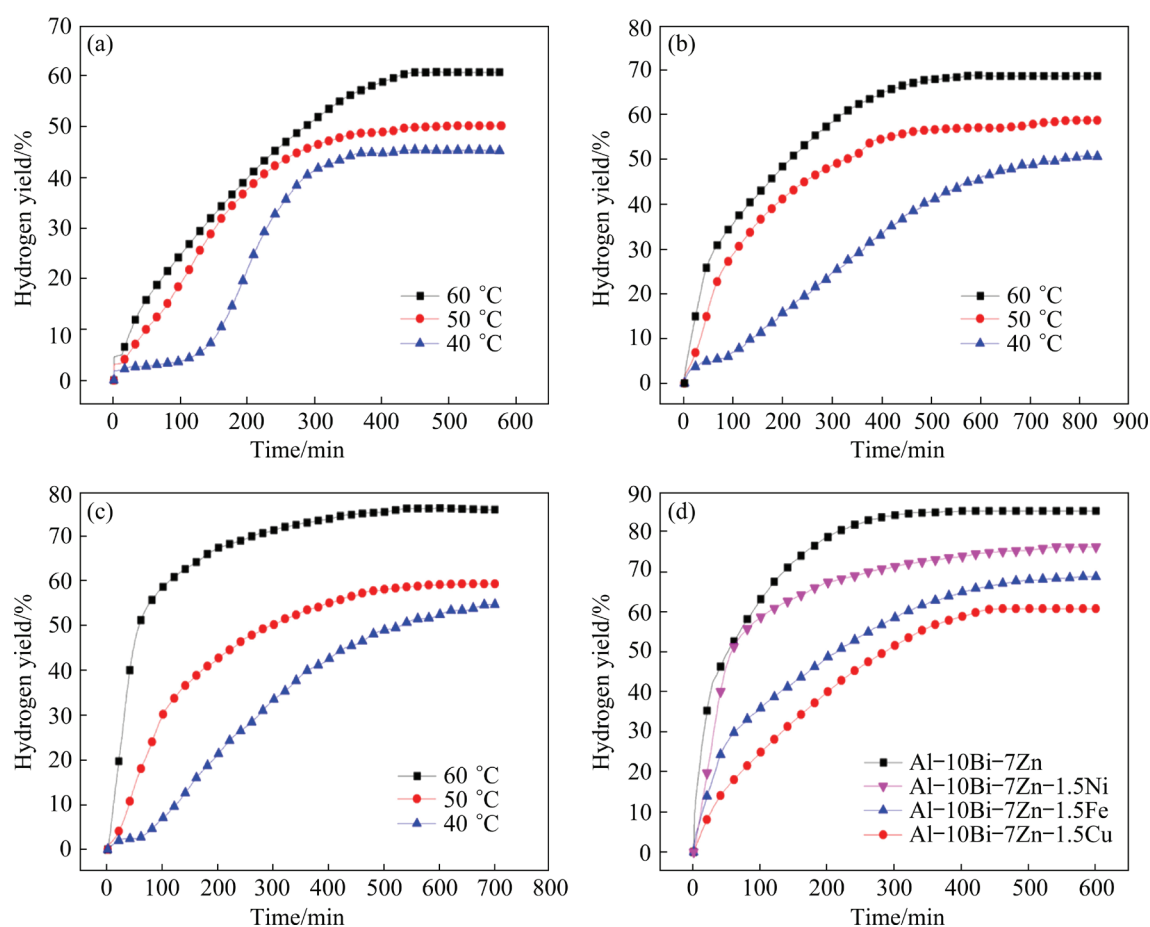


Fig. 6 Hydrogen yield of Al-10Bi-7Zn and Al-10Bi-7Zn-1.5X composite powders reacting with distilled water: (a) Al-10Bi-7Zn-1.5Cu; (b) Al-10Bi-7Zn-1.5Fe; (c) Al-10Bi-7Zn-1.5Ni; (d) Al-10Bi-7Zn; Al-10Bi-7Zn-1.5X at 60 °C

500 min. The hydrogen production curves of Al-10Bi-7Zn-1.5Fe and Al-10Bi-7Zn-1.5Ni composite powders at three temperatures have only two stages of uniform growth stage and slow growth stage. Among them, Al-10Bi-7Zn-1.5Fe can achieve a hydrogen yield of 50.7% (603.1 mL/g) within 800 min at 40 °C. As the temperature increases to 60 °C, the hydrogen yield will further increase to 68.6% (869.4 mL/g). Among the three groups of quaternary alloy composite powders, Al-10Bi-7Zn-1.5Ni has the best hydrogen production efficiency. At 40 °C, the hydrogen yield can reach 54.7% (651.2 mL/g) within 700 min. When the temperature increases to 60 °C, the hydrogen yield can further increase to 75.3% (954.1 mL/g) within 500 min. The above results show that the hydrogen production performance of quaternary alloy composite powders increases with the increase in temperature. In addition, each powder has a stable and uniform hydrogen production period in each temperature range.

Figure 6(d) shows the hydrogen production curves of Al-10Bi-7Zn ternary alloy composite powder and Al-10Bi-7Zn-1.5X (X: Cu, Fe, Ni) quaternary alloy composite powder in distilled water at 60 °C. It can be seen that the additions of Cu, Fe, and Ni can effectively slow down the hydrogen production rate, and the slowing degree from high to low is Cu, Fe and Ni. The decrease in hydrogen production and hydrogen generation rate may be due to the solid solution of the fourth component in the Al-rich phase. These elements could inhibit the cracking of the powder and reduce the reaction activity of Al, resulting in the failure of the powder to react violently with water to produce hydrogen. Compared with Al-10Bi-7Zn, the hydrogen production and hydrogen production rate of Al-10Bi-7Zn-1.5X (X: Cu, Fe, Ni) are lower, but the hydrogen production rate of quaternary alloy powder is stable, which can supply hydrogen for a long time in practical application.

Figure 7 shows the SEM images of hydrolysis

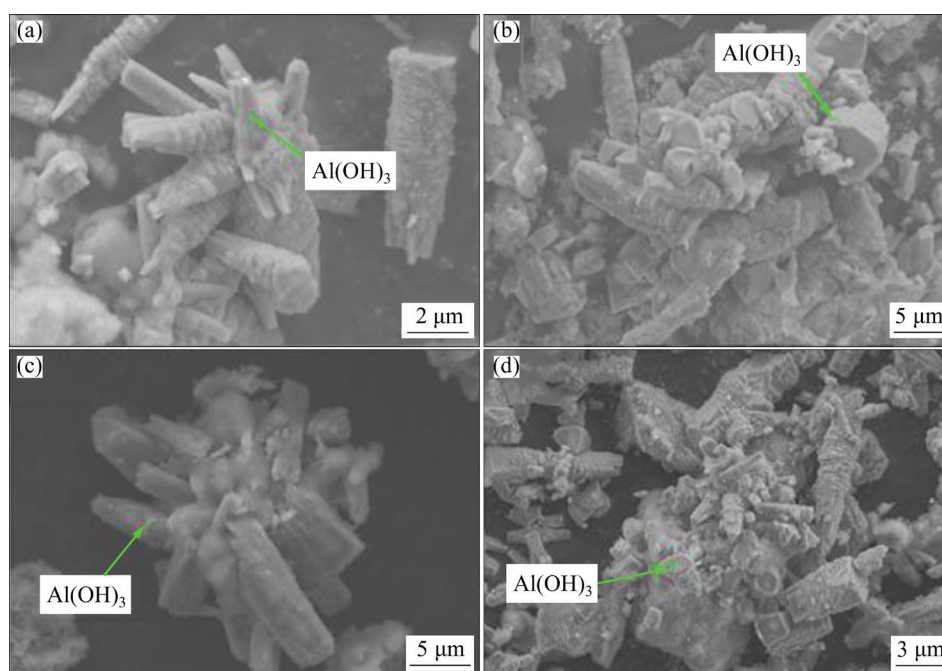


Fig. 7 SEM images of hydrolysis products in Al-10Bi-7Zn and Al-10Bi-7Zn-1.5X composite powders: (a) Al-10Bi-7Zn; (b) Al-10Bi-7Zn-1.5Cu; (c) Al-10Bi-7Zn-1.5Fe; (d) Al-10Bi-7Zn-1.5Ni

products in Al-10Bi-7Zn and Al-10Bi-7Zn-1.5X (X: Cu, Fe, Ni) composite powders. After reaction with water, the original spherical shape of the composite powders will be cracked into irregular columnar blocks from the grain boundary. As the grain boundary is the place where a large number of dislocations and prestress are enriched, the grain boundary of the Al-rich phase is easy to crack during hydrolysis. In the meantime, the microstructures of the reaction products also illustrate that water can continuously react with fresh Al through the grain boundary of the Al-rich phase during the hydrolysis reaction of composite powders. This is the reason that the composite powders can produce hydrogen continuously. In addition, although each composite powder can be broken in water, the activity of the powder fragments will ultimately determine the hydrogen production capacity of the powder.

Figure 8 shows the XRD patterns of hydrolysis products in Al-10Bi-7Zn and Al-10Bi-7Zn-1.5X (X: Cu, Fe, Ni) composite powders, and the characteristic peak of Al, Al(OH)₃, and Bi can be detected in the patterns. The characteristic peaks of Al and Al(OH)₃ suggest that Al hydrolyzes with water to produce hydrogen, and there is still a small amount of Al that does not react completely. The existence of Bi characteristic peak indicates that Bi

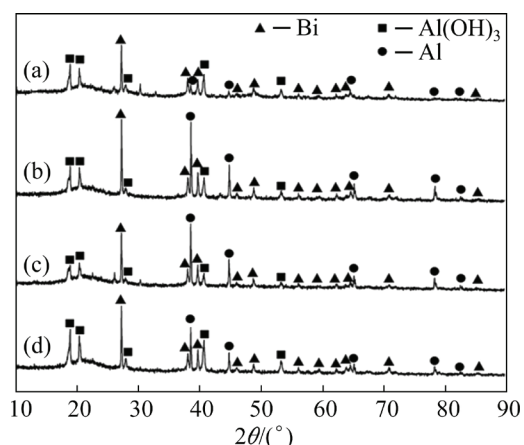


Fig. 8 XRD patterns of hydrolysis products in Al-10Bi-7Zn and Al-10Bi-7Zn-1.5X composite powders: (a) Al-10Bi-7Zn; (b) Al-10Bi-7Zn-1.5Cu; (c) Al-10Bi-7Zn-1.5Fe; (d) Al-10Bi-7Zn-1.5Ni

does not react with distilled water. No Zn, Cu, Fe and Ni characteristic peaks were measured. It may be due to the large solid solubility of Zn, Cu, Fe and Ni in Al.

3.4 Oxidation resistance performance

The easy passivation of Al metal surface and deliquescence in the air has always been the main obstacles to the development of Al and its alloys for hydrogen production [40]. Therefore, it is very important to study the oxidation resistance of

Al-based composite powder in the air. In order to study the oxidation resistance of Al-based composite powder, Al-10Bi-7Zn, Al-10Bi-7Zn-1.5Cu, Al-10Bi-7Zn-1.5Fe, and Al-10Bi-7Zn-1.5Ni were stored in a constant temperature and humidity chamber (30 °C, 60% RH) for 0, 3, 5, and 7 d. Figure 9 shows the SEM images of four composite powders after storage for different time. It can be seen that Al-10Bi-7Zn composite powders after 3 d of storage, due to their contact with oxygen and moisture in the air, the powders no longer maintain the initial morphology, and the cracks propagate along the grain boundary, causing the powders to become ruptured and passivated (Fig. 9(a₁)). However, the morphology of Al-10Bi-7Zn-1.5X (X: Cu, Fe, Ni) composite powders remained basically unchanged after 3 d of storage, only a small amount of Bi-rich phases distributed in dots on the powder surface fell off (Figs. 9(b₁–d₁)). After 7 d, cracks appear on the surface of the Al-10Bi-7Zn-1.5X (X: Cu, Fe, Ni) composite powders along the grain boundary (Figs. 9(b₃–d₃)). In comparison, Al-10Bi-7Zn composite powders are broken along the grain boundary completely

(Fig. 9(a₃)) in 7 d. The reason for these differences may be that the addition of the fourth component in the composite powders can stabilize the Al matrix by solid solution. Figure 10 shows the cross-sections of Al-10Bi-7Zn-1.5X (X: Cu, Fe, Ni) composite powders after being stored (30 °C, 60% RH) for 7 d. Significantly, after 7 d of storage, a passivation layer will be formed on the surface of the quaternary composite powders. This passivation layer is the key to keeping the morphology of the composite powders unchanged in the air for a long time.

Figure 11 shows the hydrogen production performance of four powders reacting with distilled water at 60 °C after storage for 3, 5, and 7 d under the same conditions (30 °C, 60% RH). The results show that the hydrogen production capacity of Al-10Bi-7Zn composite powder reduced to 37.8% (478.1 mL/g) after 7 d of storage. In the meantime, all the quaternary alloy powders have excellent oxidation resistance. Especially, even after 7 d of storage, Al-10Bi-7Zn-1.5Ni can still maintain a hydrogen yield of 57.9% (733.7 mL/g) within 1500 min, showing satisfactory antioxidant capacity.

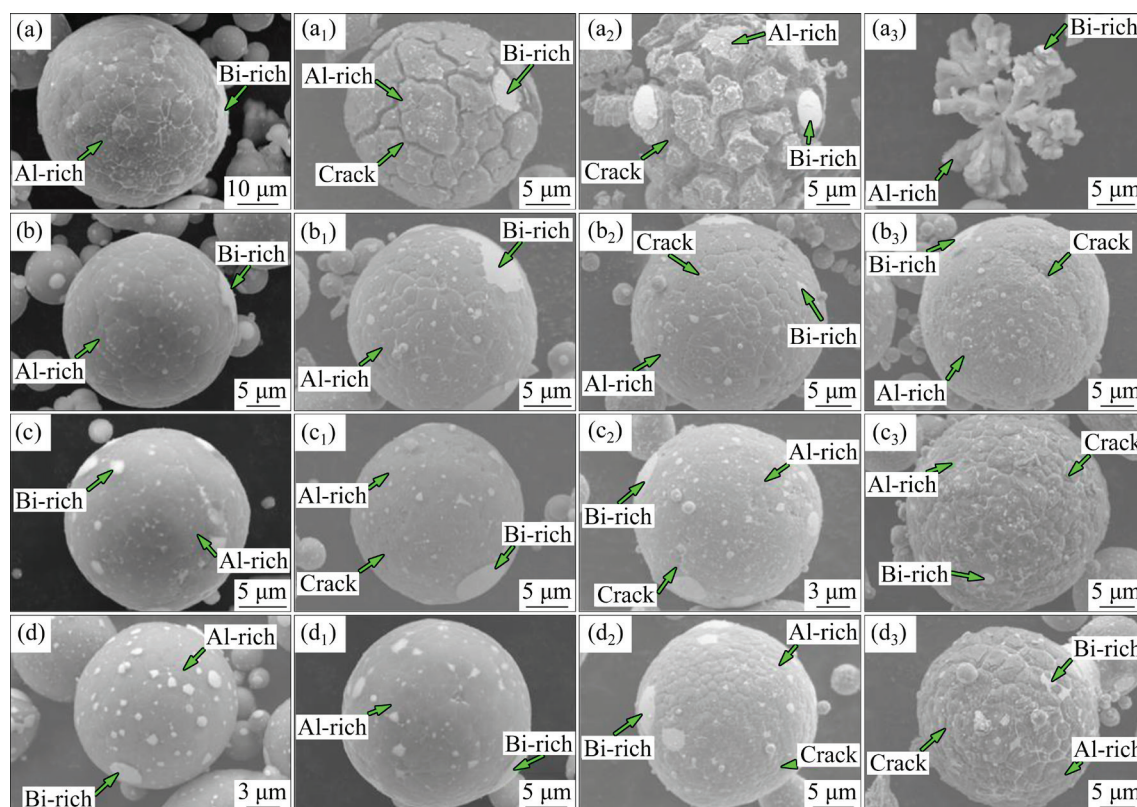


Fig. 9 SEM images of Al-10Bi-7Zn (a–a₃), Al-10Bi-7Zn-1.5Cu (b–b₃), Al-10Bi-7Zn-1.5Fe (c–c₃), and Al-10Bi-7Zn-1.5Ni (d–d₃) composite powders after being stored (30 °C, 60% RH) for 0 d (a–d), 3 d (a₁–d₁), 5 d (a₂–d₂) and 7 d (a₃–d₃)

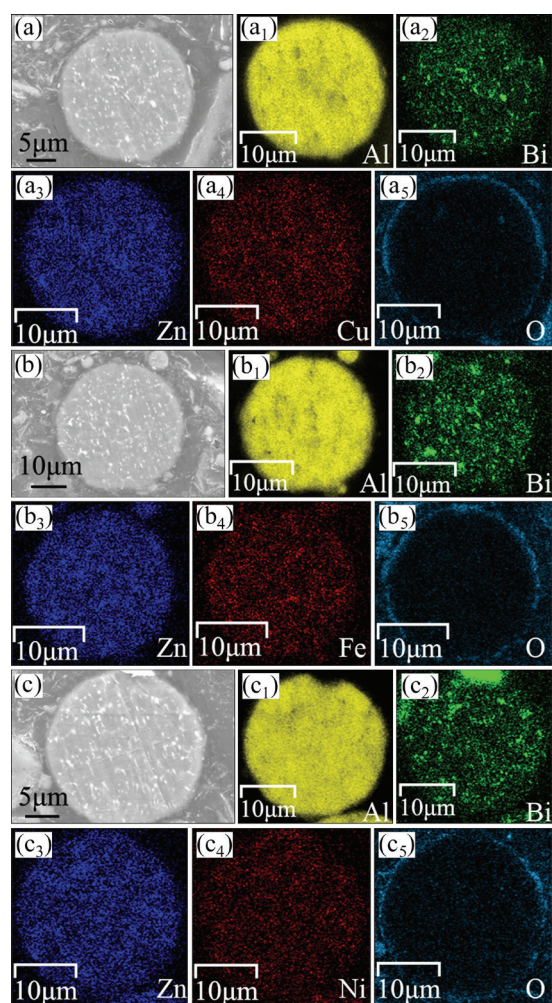


Fig. 10 SEM images and EDS mappings of cross-sections of Al-10Bi-7Zn-1.5X composite powders after being stored (30 °C, 60% RH) for 7 d: (a–a₅) Al-10Bi-7Zn-1.5Cu; (b–b₅) Al-10Bi-7Zn-1.5Fe; (c–c₅) Al-10Bi-7Zn-1.5Ni

3.5 Mechanism

In previous studies, WANG et al [26] have explained the hydrolysis reaction process of Al-Bi-Zn ternary alloy composite powder, Al-Bi-Zn composite powder after being reacted in the water was typical morphology of popcorn formula. The hydrolysis reaction process of Al-10Bi-7Zn-1.5X (X: Cu, Fe, Ni) quaternary alloy composite powders is similar to that of Al-Bi-Zn ternary alloy composite powder. A schematic illustration of the reaction mechanisms of the Al-10Bi-7Zn-1.5X (X: Cu, Fe, Ni) composite powders reacting with distilled water at 60 °C is presented in Fig. 12. After the composite powder contacts with water, its surface quickly reacts with water to generate aluminum hydroxide and

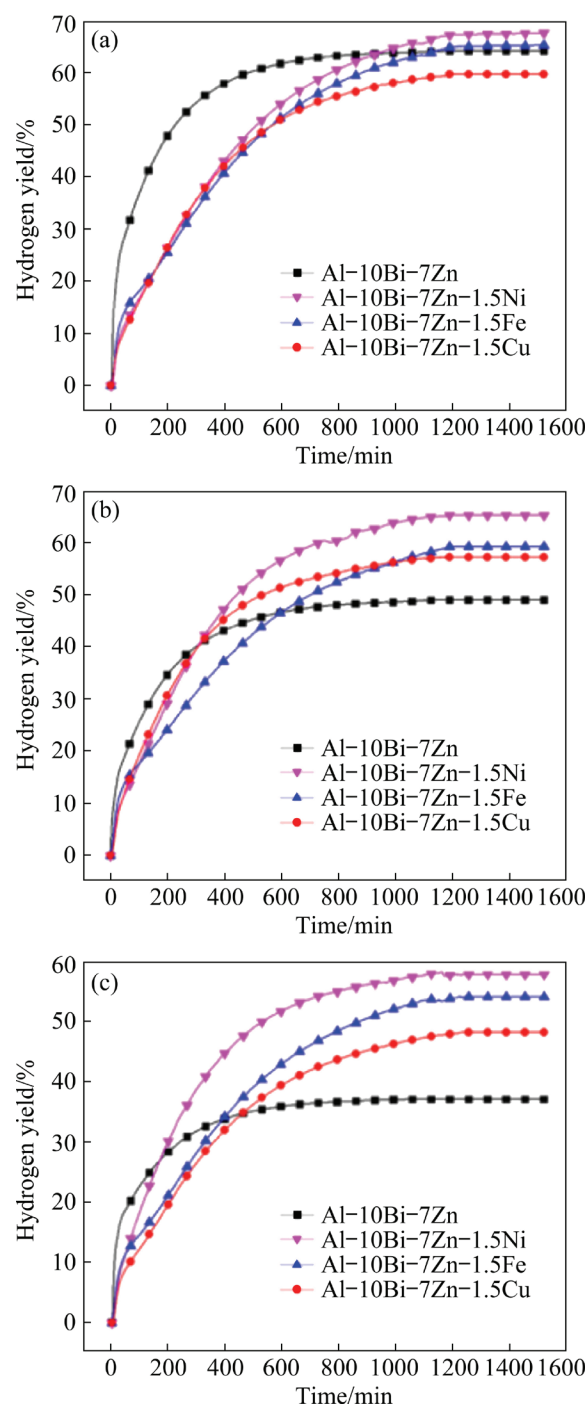
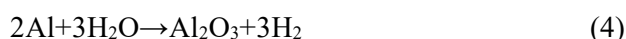
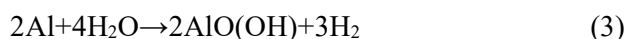
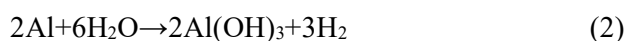


Fig. 11 Hydrogen yields of Al-10Bi-7Zn and Al-10Bi-7Zn-1.5X composite powders reacting with 60 °C distilled water after being stored (30 °C and 60% RH) for different time: (a) 3 d; (b) 5 d; (c) 7 d

hydrogen. And the reaction of Al hydrolysis can be expressed as [41]



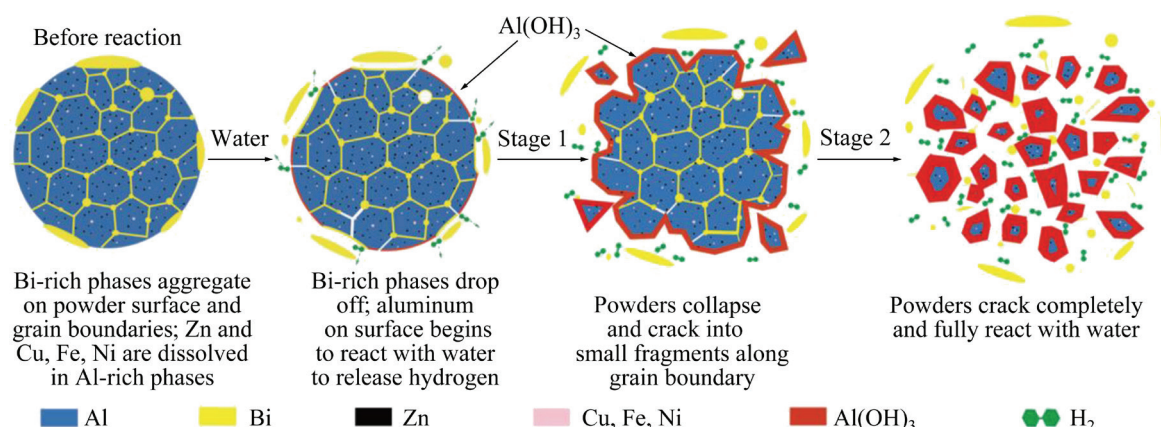


Fig. 12 Schematic illustration of reaction mechanisms of Al–10Bi–7Zn–1.5X composite powders reacting with distilled water at 60 °C

Then, due to the loose connection between the Bi-rich phase and Al-rich phase on the powder surface, water infiltrates into the gap between the two phases and hydrolyzes with Al (Stage 1). The hydrogen bubbles generated by the Al hydrolysis reaction led to the expansion of the alloy powder, the Bi-rich phase on the powder surface and the Bi-rich phase at the powder grain boundary continue to fall off with the reaction, and the fresh Al continues to be exposed to promote the continuous and rapid hydrolysis reaction (Stage 2). Finally, the spherical structure of the powder collapsed and cracked into small fragments along the grain boundary, which increased the contact area between Al and water, and the hydrolysis reaction continued to occur.

It is worth noting that in the Al–Bi–Zn-base composite powders, through the Al matrix is cracked into small fragments, they also cannot completely react with water. This is confirmed by the XRD patterns of composite powders hydrolysis products in Fig. 8, in which the characteristic peaks of Al are still identified in addition to the characteristic peaks of $\text{Al}(\text{OH})_3$ and Bi. It indicates that some Al matrix is not reacted with water under the coating of $\text{Al}(\text{OH})_3$. As shown in SEM images (Fig. 7), the Al matrix that has not yet reacted with water may exist inside the irregular columnar blocks. Due to the additions of the fourth component (Cu, Fe, Ni) stabilizing the Al matrix, more Al matrix does not participate in hydrolysis reaction in Al–10Bi–7Zn–1.5X (X: Cu, Fe, Ni) composite powders. This is the reason that the hydrogen production capacity of Al–10Bi–7Zn–

1.5X (X: Cu, Fe, Ni) quaternary composite powders are weaker than that of Al–10Bi–7Zn composite powder, as shown in Fig. 6.

In recent years, CHEN et al [11] reported a kind of Al alloy powder that reacts with low-temperature water vapor. Their investigation provides a theoretical basis for the deactivation of Al–Bi–Zn composite powder in the air. In this study, the Al–10Bi–7Zn–1.5X (X: Cu, Fe, Ni) composite powders retain high stability in the air. As shown in Fig. 9, after introducing Cu, Fe or Ni to Al–10Bi–7Zn composite powder, powders hardly crack in the air. This is the reason that Al–10Bi–7Zn–1.5X (X: Cu, Fe, Ni) composite powders can still maintain high hydrogen yield after 7 d of storage (30 °C, 60% RH).

4 Conclusions

(1) The unit hydrogen production of Al–10Bi–7Zn–1.5X (X: Cu, Fe, Ni) composite powders is less than Al–10Bi–7Zn composite powder when reacting with distilled water at 60 °C. Al–10Bi–7Zn–1.5Ni composite powder exhibits the best performance with the hydrogen generation yield of 75.3% (954.1 mL/g) within 500 min in the quaternary composite powders system.

(2) The hydrogen production rates of Al–Bi–Zn-base composite powders become more stable and milder due to the additions of the fourth component (Cu, Fe, Ni) resulted in the strengthen of the matrix.

(3) The additions of high melting point metal (Cu, Fe, Ni) can inhibit Al–10Bi–7Zn composite

powder cracking in the air and enhance the oxidation resistance of Al–Bi–Zn-base composite powders. After 7 d of storage (30 °C, 60% RH), the hydrogen production capacity of all quaternary composite powders exceeded that of Al–10Bi–7Zn composite powder. In particular, Al–10Bi–7Zn–1.5Ni can still maintain a hydrogen yield of 57.9% (733.7 mL/g) within 1500 min when reacting with distilled water at 60 °C.

CRedit authorship contribution statement

Cui-ping WANG: Conceptualization, Methodology, Supervision, Funding acquisition; **Fang-zheng YU:** Investigation, Writing – Original draft, Writing – Review & editing; **Yan HUANG:** Investigation; **Ming-shuai WANG:** Investigation, Writing – Review & editing; **Rui DENG:** Writing – Review & editing; **Yi-hui GUO:** Data curation; **Jin-bin ZHANG:** Data curation; **Shui-yuan YANG:** Writing – Review & editing; **Xing-jun LIU:** Conceptualization, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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一种能温和产氢且具有高活性保持能力的 Al–Bi–Zn 基复合粉体

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摘 要: 通过相图计算和气体雾化的方法, 设计并制备 Al–10Bi–7Zn 和 Al–10Bi–7Zn–1.5X (X: Cu, Fe, Ni) (质量分数, %) 复合粉体。研究 Cu、Fe 和 Ni 对 Al–Bi–Zn 基复合粉体水解制氢性能的影响。通过 X 射线衍射 (XRD) 和扫描电子显微镜 (SEM) 以及能量色散谱 (EDS) 分析对粉体的组成和形貌进行表征。水解制氢性能测试结果表明, 添加 Cu、Fe 或 Ni 可以改变 Al–10Bi–7Zn 三元合金复合粉体的制氢速率, 并且提高其抗氧化性能。在四元复合粉体体系中, Al–10Bi–7Zn–1.5Ni 表现出最佳的制氢性能, 在 60 °C 下与蒸馏水反应时, 500 min 内的产氢率为 75.3% (954.1 mL/g), 在储存 7 d 后 (30 °C, 相对湿度 60%), 1500 min 内保持 57.9% (733.7 mL/g) 的产氢率。此外, 机理研究表明, 在 Al–Bi–Zn 基复合粉体中添加 Cu、Fe 或 Ni 可以稳定 Al 基体, 抑制复合粉体在空气中的开裂, 保持粉体的高活性。

关键词: 铝合金; 气雾化; 水解反应; 制氢; 抗氧化

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