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ARTICLE

Influence of Ball-Milling on the Structure and Hydrogen Absorption-desorption Behavior of Zr-Cu-Al-Ni Metallic Glass Powders

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Abstract: The influence of ball-milling on the structure and hydrogen absorption-desorption behavior of $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders produced by gas atomization were studied. The as-atomized metallic glass powders were ball-milled for 80 h. It is found that the powders remain amorphous state after the ball-milling process. The effects of ball-milling on the hydrogen absorption-desorption behavior of the metallic glass powders were measured with an automatic Sieverts apparatus. After the ball-milling, the hydrogen absorption behavior of the metallic glass powders is improved. In addition, the hydrogen absorption capacity of the ball-milled metallic glass powders increases to 2.66 wt% (H/M≈1.9) from 0.96 wt% (H/M≈0.7) of the as-atomized metallic glass powders. However, the hydrogen desorption behavior of the ball-milled metallic glass powders is still poor due to the formation of very stable hydride.

Key words: ball-milling; structure; hydrogen absorption-desorption behavior; metallic glass powders

Due to their unique physical and chemical properties different from traditional crystalline metals, metallic glasses own widely potential applications and attract tremendous attention[1-4]. Among these, Zr-based metallic glasses show high glass-forming ability as well as outstanding properties, which make them a category of promising structural as well as functional materials for practical applications[5-7].

Zr-Cu-Al-Ni metallic glass systems consist of a combination of early and late transition metals. Because of the strong hydrogen affinity of Zr and Al, and the catalytic activity of Ni on hydrogen absorption-desorption process, Zr-Cu-Al-Ni metallic glass systems are regarded as promising candidates for hydrogen storage applications[8,9]. In fact, it has been found that by electrochemical charging, the Zr-Cu-Al-Ni metallic glasses can absorb a large amount of hydrogen up to a hydrogen per metal atom content (H/M) of 1.6[10,11]. Because of the very high glass-forming ability, Zr-based metallic glass powders can be easily prepared by gas atomization, which is very beneficial to their industrialized applications[12,13]. Hence we prepared $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders by a gas atomization method to study their gaseous hydrogen storage properties. However, in our experimental work, we found that the gas hydrogen absorption-desorption kinetics of the as-atomized Zr-based metallic glasses powders are very slow, which might be due to the existence of surface barrier[14,15]. According to the work of Inoue et al.[16], Zr-Cu-Al-Ni metallic glass shows high phase stability against deformation during ball-milling process, which means that the surface structure as well as the hydrogen storage behavior of Zr-Cu-Al-Ni metallic glasses can be changed by ball-milling, while their amorphous phase structure still remains.

In the present paper, $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders were produced by gas atomization. Then, the as-atomized powders were subjected to surface treatments by ball-milling in order to improve their hydrogen absorption-desorption properties. The influence of ball-milling on the structure and hydrogen absorption-desorption behavior of $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders were investigated.

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1 Experiment

$Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders with particle size distribution mainly between 50~150 μm were produced by argon gas atomization. The as-atomized metallic glass powders were ball-milled for 80 h by a planetary ball-mill in an argon atmosphere with a container and balls made of hardened stainless steel. The rotational speed was 250 r/min and the ball to powders weight ratio was 20:1.

The morphologies of the as-atomized and ball-milled metallic glass powders were characterized by scanning electron microscopy (SEM). The phase structure of the metallic glass powders were investigated by X-ray diffraction (XRD) with Cu Kα radiation. The thermal analysis of the metallic glass powders were performed by differential scanning calorimetry (DSC) with a heating rate of 20 K/min in an argon atmosphere.

The hydrogen absorption-desorption behaviors of the metallic glass powders were measured by an automatic Sieverts apparatus at 623 K. The hydrogen absorption and desorption kinetics measurements were carried out with the initial hydrogen pressures of 7 MPa and 0.01 MPa, respectively. The phase structure and thermodynamic properties of the metallic glass powders after the hydrogen absorption and desorption were also examined by XRD and DSC, respectively.

2 Results and Discussion

The morphology of the as-atomized $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders is shown in Fig. 1a. It can be seen that most of the as-atomized metallic glass powders are spherical or nearly spherical. The surfaces of the powders are relatively smooth. However, the large-sized powders have small adhering satellites. Fig. 1b shows the surface morphology of the ball-milled $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders. It can be seen that the surfaces of the milled powders are very rough compared to the unmilled ones. However, their shapes and sizes are nearly unchanged. It is also found that the adhering satellites disappear after the ball-milling.

Fig.2a shows the XRD patterns of the as-atomized and ball-milled $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders. Both the patterns own a broad diffuse peak without sharp diffraction peaks, indicating no crystallization has yet taken place in the metallic glass powders after the ball-milling. However, as shown in Fig. 2b, a little difference can be found between the DSC curves of the as-atomized and ball-milled metallic glass powders. The glass transition temperature (T_g) increases and the supercooled liquid region ΔT_x ($\Delta T_x = T_x - T_g$) decreases after the ball-milling. According to the work of Inoue et al.[16], a small amount of Fe atoms will be diffused into the metallic glass powders during ball-milling process. The introduction of minor Fe will affect the structure and thermodynamic properties of the ball-milled metallic glass

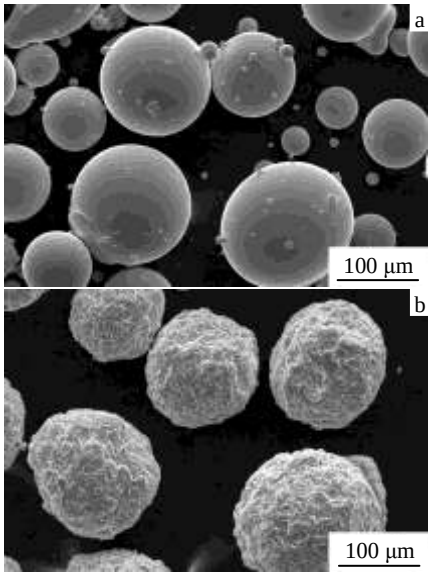
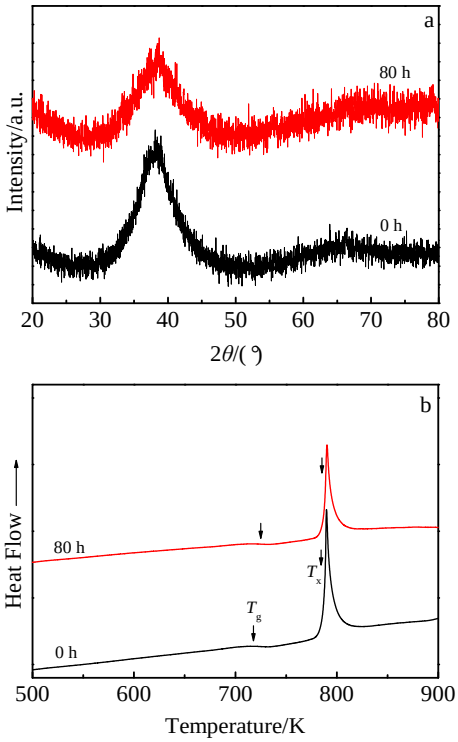


Fig.1 SEM images of the $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders: (a) as-atomized and (b) ball-milled



Time/h	T_g/K	T_x/K	ΔT_x/K
0	722.2	787.5	65.3
80	728.1	787.5	59.4

Fig.2 XRD patterns (a) and DSC curves (b) of the as-atomized (0 h) and ball-milled (80 h) $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders

powders. But the onset crystallization temperatures (T_x) keep the same and both the crystallization peaks are sharp as shown in Fig.2b, indicating the amorphous state of the metallic glass powders remains after the ball-milling. The above results show that the as-atomized $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders own excellent amorphous phase stability against deformation during ball-milling process.

Fig.3a shows the hydrogen absorption kinetics curves of the as-atomized and ball-milled $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders. It can be observed that the hydrogen absorption kinetics of the metallic glass powders is apparently accelerated after the ball-milling. Additionally, the hydrogen absorption capacity of the ball-milled metallic glass powders increases up to 2.66 wt% (H/M≈1.9) from 0.96 wt% (H/M≈0.7) of the as-atomized metallic glass powders. As-mentioned above, very rough surfaces formed after the ball-milling. As a result, the surface area increases and the surface oxide layers are also broken, which are helpful to the improvement of hydrogen absorption behavior. Meanwhile, the deformation caused by ball-milling will take a large number of micro-cracks into the metallic glass powders, which will contribute to improving the hydrogen storage properties too[17,18]. The hydrogen desorption kinetics curves of the as-atomized and ball-milled metallic glass powders are shown in Fig.3b. It is seen that the hydrogen desorption kinetics of $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders is very slow. The hydrogen desorption kinetics can not be improved by ball-milling, which may be due to the formation of very

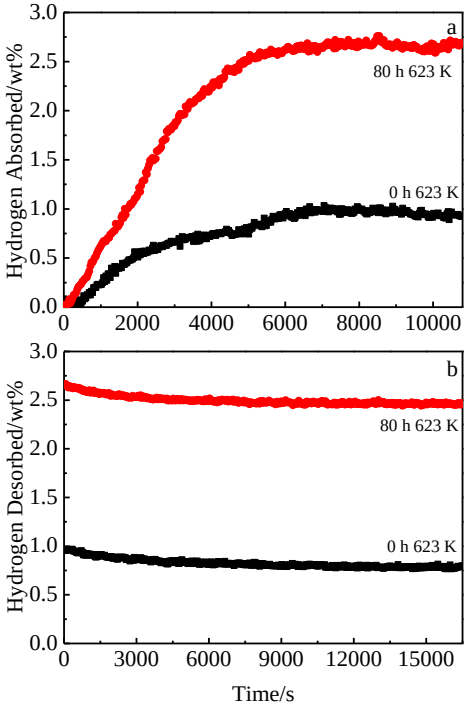


Fig.3 Hydrogen absorption (a) and desorption (b) kinetics curves of as-atomized (0 h) and ball-milled (80 h) $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders at the temperature of 623 K

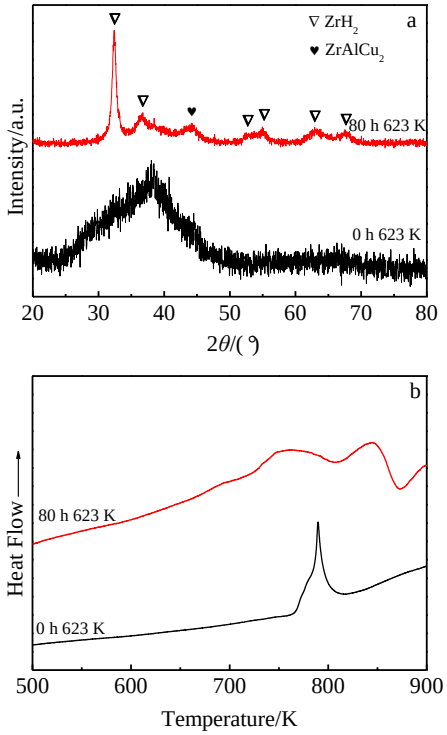


Fig.4 XRD patterns (a) and DSC curves (b) of the as-atomized (0 h) and ball-milled (80 h) $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders after the hydrogen absorption-desorption process at the temperature of 623 K

stable hydrides in $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders. To reveal the hydrogen induced structural changes, we further examined the XRD and DSC of $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass powders after the hydrogen absorption-desorption process. As shown in Fig.4a, it can be seen that the as-atomized metallic glass powders remain amorphous state after the hydrogen absorption-desorption process, while the ball-milled metallic glass powders crystallize seriously and a large amount of Zr-hydride forms in them. The DSC curves of the as-atomized and ball-milled metallic glass powders after the hydrogen absorption- desorption process are shown in Fig. 4b. Compared with the sharp crystallization peak of the as-atomized metallic glass powders, there are two broad exothermic peaks on the curve of the ball-milled metallic glass powders. According to the work of Gebert et al.[19], the two broad exothermic peaks stand for the hydrogen desorption processes occurring under phase transformations of ε-Zr-hydride to δ-Zr-hydride and δ-Zr-hydride to (α+β)-Zr-hydride, respectively. It is observed that the initial temperatures of these phase transformations are higher than 730 K. The high temperatures needed for the phase transformations of Zr-hydride indicate that the hydrogen desorption of the ball-milled metallic glass powders is difficult at 623 K. The present results show that the hydrogen desorption kinetics of $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ metallic glass

powders is restricted by the stability of the hydrides, not by the surface structure.

3 Conclusions

1) The as-atomized metallic glass powders own excellent amorphous phase stability against deformation during ball-milling process, and the powders remain amorphous after the ball-milling.

2) The hydrogen absorption capacity of the ball-milled metallic glass powders increases to 2.66 wt% (H/M≈1.9).

3) The formation of very stable hydrides in the metallic glass powders should be the main reason why the hydrogen desorption kinetics can not be improved by ball-milling.

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球磨对 Zr-Cu-Al-Ni 金属玻璃粉末结构与吸放氢性能的影响

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摘 要：研究了球磨对气雾化法所制备的 $Zr_{50.7}Cu_{28}Al_{12.3}Ni_9$ 金属玻璃粉末结构与吸放氢性能的影响。气雾化的金属玻璃粉末在经过 80 h 的球磨后，仍呈现为非晶态。球磨对金属玻璃粉末吸放氢性能的影响在一台全自动 Sieverts 装置上进行了测量。球磨之后，金属玻璃粉末的吸氢性能获得提升，粉末的饱和吸氢质量分数从雾化态的 0.96 % (H/M≈0.7)提升至了球磨后的 2.66% (H/M≈1.9)。然而，由于吸氢后金属玻璃粉末内部生成稳定的氢化物相，使得球磨后的金属玻璃粉末的放氢性能未能获得提升。

关键词：球磨; 结构; 吸放氢性能; 金属玻璃粉末

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