

Hydriding properties of amorphous Ni–B alloy studied by DSC and thermogravimetry

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Received 7 August 1998; accepted 14 October 1998

Abstract

The hydrogenation behaviour of melt-spun Ni_{81.5}B_{18.5} amorphous alloy was studied by means of differential scanning calorimetry (DSC) and thermogravimetry (TG) and compared with the hydriding properties of a Fe–B–Si glass. It was found that the amorphous Ni–B alloy absorbs larger amounts of hydrogen than the Fe–B–Si glass, as the initial kinetics of hydrogen absorption and desorption of both the alloys are comparable. Hydrogen absorption and desorption reactions in Ni–B were observed to proceed with similar rates at ca. 300 K. The hydrogen desorption is revealed in DSC as an endothermic peak in the 350–450 K range, preceding the crystallization peak of the amorphous alloy. The enthalpy of hydrogen desorption ($\Delta H_{\text{des}}=22$ kJ/mol H₂) for Ni–B was found to be smaller than that for the Fe–B–Si glass, which finding is in contrast to the results on hydrogen diffusion in crystalline α Fe and Fe-based alloys and Ni and Ni-based alloys. The hydrogen desorption temperature and enthalpy for Ni_{81.5}B_{18.5} were found to be independent of the amount of hydrogen absorbed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ni–B alloy; Metallic glass; Hydrogenation; Differential scanning calorimetry; Thermogravimetry

1. Introduction

Hydrogen in amorphous alloys has been a subject of numerous studies in the recent years. Hydrogen has high solubility and mobility (diffusivity) in many crystalline and amorphous alloys and even at small concentrations it can cause significant changes in some physicochemical, mechanical and magnetic properties. Although metallic glasses are supposed to show reduced tendency for disintegration during hydrogen absorption/desorption, it has been reported that they are also susceptible to hydrogen embrittlement [1]. Hydrogen embrittlement of Ni and its alloys has been a subject of intensive work in the last decades

as well. Hydrogen often causes a decrease in the thermal stability of glass, which reduction of the crystallization temperature for some amorphous alloys was found to be >200 K (e.g. in case of Cu–Ti [2,3] and Cu–Ti–Al [4] metallic glasses).

The interest in hydrogenated metallic glasses appears also because of the possibility of using them as hydrogen storage materials. Some amorphous alloys can absorb (in solid solution or as hydrides) larger amounts of hydrogen than the crystalline alloys. Besides, for storage of fuel hydrogen, metal hydrides (including hydrogenated metallic glasses) can be used to store thermal energy or electrochemical energy (as a cathode of a battery). Because of these reasons, studies on diffusion of hydrogen in amorphous alloys have been undertaken [1,5,6]. Studies on hydrogen diffu-

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sion in amorphous and nanocrystalline Ni-based alloys have been also carried out in recent years [1,5,7,8]. Hydrogen can also be used as a probe in the analysis and investigation of structural disorder in the amorphous materials [5,6].

Hara et al. [1] have studied the hydrogen diffusivity in $\text{Ni}_{77.5}\text{Si}_{7.9}\text{B}_{14.6}$ amorphous alloy in comparison with those in the corresponding crystallized alloys. They found that the diffusivity of hydrogen changed with the ageing treatment, depending on the microstructure produced by ageing. Santos et al. [5] have investigated the hydrogen diffusivity and solubility in crystalline and amorphous Fe-based and Ni-based alloys. They found that the amorphous alloys possess greater capacity to dissolve hydrogen in solid solutions compared with their crystalline counterparts. Palumbo et al. [8] have provided evidence for the existence of distinct triple junctions, grain boundary and lattice paths for hydrogen diffusion in nanocrystalline Ni. Arantes et al. [7] have reported that the hydrogen permeation in nanocrystalline Ni is remarkably larger in comparison with microcrystalline Ni, due to an increase of both, hydrogen solubility and hydrogen diffusivity in the former material.

In the present work, an amorphous $\text{Ni}_{81.5}\text{B}_{18.5}$ alloy, rapidly quenched from the melt, was charged electrolytically with hydrogen and the hydriding/dehydriding properties of this alloy were studied from both the thermodynamic and kinetic aspect by means of thermogravimetry and DSC.

2. Experimental methods

Amorphous $\text{Ni}_{81.5}\text{B}_{18.5}$ ribbons were prepared by planar-flow casting technique onto a copper wheel with surface velocity of ca. 30 m/s. The sample width and thickness were 7.10^{-3} m and 35.10^{-6} m, respectively. Hydrogenation of the as-quenched amorphous ribbons was carried out electrolytically under galvanostatic conditions, at a current density of 5–6 mA/cm² in 1 N H_2SO_4 aqueous solution, containing an inhibiting addition Na_2HAsO_3 (4 mg/l). The Pt-wire anode in the form of a spiral, was located symmetrically to the cathodic polarized ribbon (3.10^{-2} m long). The hydrogen content of hydrogenated samples was determined by weight measurements using a Perkin–Elmer thermobalance TFS-2. The hydrogen

desorption as well as the influence of hydrogen on the thermal stability of the glass were studied by means of a Perkin–Elmer DSC-2C differential scanning calorimeter under an atmosphere of pure argon. The amorphicity and structure of the as-quenched and hydrogenized glasses, as well as partially and fully crystallized samples with, and without, hydrogen were characterized by X-ray diffraction, using $\text{CuK}\alpha$ radiation.

3. Results and discussion

X-ray diffraction analysis of the as-quenched and hydrogenated $\text{Ni}_{81.5}\text{B}_{18.5}$ ribbons (with, and without, hydrogen) did not show any traces of crystallinity. A change in the first diffraction halo (typical for amorphous structure) was also not observed after hydrogenation.

Typical thermogravimetric (TG) curves of hydrogenated amorphous Ni–B samples (at different hydrogenation times) are presented in Fig. 1. The hydrogen content increases with the time of H-charging and, finally, reaches up to 0.35–0.40 wt.% for longer hydrogenation times, as shown in Figs. 1 and 2. Saturation of the hydrogen content with the hydrogenation time was observed at times of hydrogen charging longer than $t \geq 4$ h. Although the hydrogen

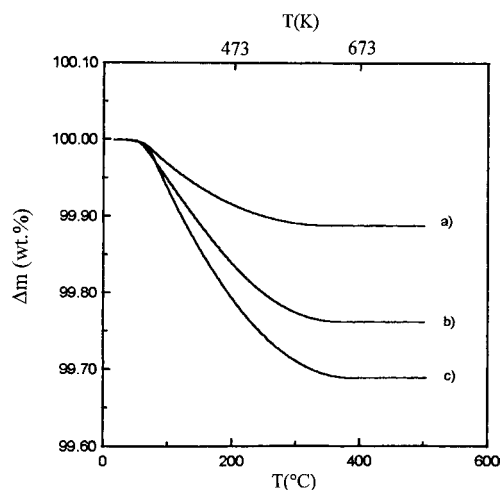


Fig. 1. Thermogravimetric (TG) curves of hydrogenated amorphous $\text{Ni}_{81.5}\text{B}_{18.5}$ alloys: (a) 30, (b) 75 and (c) 150 min hydrogen charging.

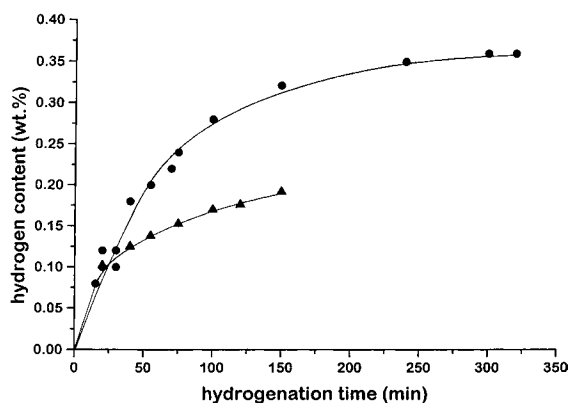


Fig. 2. Hydrogen content during hydrogenation at constant current density (●, Ni_{81.5}B_{18.5}; and ▲, Fe₇₉B₁₄Si₇).

content of the alloys hydrogenated different times is different, the dehydrogenating reaction for all samples starts at ca. 350 K.

In Fig. 2, the hydrogen content as a function of the hydrogenation time for the amorphous Fe₇₉B₁₄Si₇ alloy (obtained in our previous study [9] at nearly the same charging conditions) is also plotted, in order to compare the hydrogenation kinetics of both the amorphous alloys (Ni-based and Fe-based). It is clearly seen that the hydrogen concentration in both glasses increases with time, as Ni–B glass shows higher hydrogen absorption capacity. Both these metallic glasses show fast initial kinetics of hydrogen absorption. For the Fe–B–Si glass, after the initial fast H-absorption reaction (ca. 20–25 min) the total amount of hydrogen shows a tendency of saturation, reaching a value of 0.19 wt.% H at 150 min of hydrogenation. In the case of the Ni–B amorphous alloy, the first period of rapid H-absorption is longer (ca. 50 min), but the initial rates of hydriding for both the glasses are comparable. The higher H-content in the Ni–B glass is obviously due to the higher hydrogen solubility in Ni and Ni-based alloys than in α Fe and Fe-based alloys.

Whereas for Fe–B–Si glasses the hydrogen concentration increases with increasing current density [9], in the case of Ni–B alloy such a dependence was not found in the range of current densities from 5 to 50 mA/cm². A similar result has been obtained for the Ni_{77.5}Si_{7.9}B_{14.6} amorphous alloy [1], where the effect of the current density on the diffusivity of hydrogen was studied by means of the electrochemical

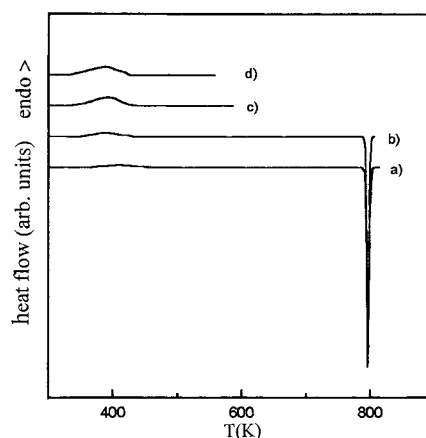


Fig. 3. Typical DSC-curves of amorphous Ni–B alloys with different H-content: (a) 0.08, (b) 0.12, (c) 0.28 and (d) 0.32 wt.% H.

permeation technique and it was found that the diffusivity of hydrogen is independent on the current density in the 10–100 mA/cm² range. The effect of temperature (in the 290–320 K range) on the hydrogen absorption in Ni–B was found to be insignificant as well.

Fig. 3 shows typical DSC curves of Ni_{81.5}B_{18.5} amorphous alloy with different hydrogen contents. Hydrogen has no influence on the thermal stability of the glass as well as on the enthalpy and kinetics of crystallization (in this case, it is a eutectic-type crystallization), which is due to the evolution of the absorbed hydrogen before the crystallization can occur (Fig. 3(a and b)). All DSC curves of hydrogenated Ni–B samples show an endothermic effect (peaks) in the 350–450 K range due to desorption of hydrogen. The enthalpy of hydrogen desorption ΔH_{des} (calculated in cal/g alloy) at different hydrogenation times, determined from the endothermic peaks is plotted in Fig. 4. Similar to the hydrogen concentration curve (Fig. 2), ΔH_{des} (quantitative measure of the absorbed hydrogen content) increases with increasing time, reaching a value of 11 cal/g alloy for a hydrogenation time $t=150$ min. It has to be mentioned that saturation of ΔH_{des} was not observed for the hydrogenation times studied. In the same figure, the data from the hydrogen absorption/desorption measurements on Fe₇₉B₁₄Si₇, obtained in our previous study [9] at similar times and charging current densities, are also presented. The enthalpies of hydrogen

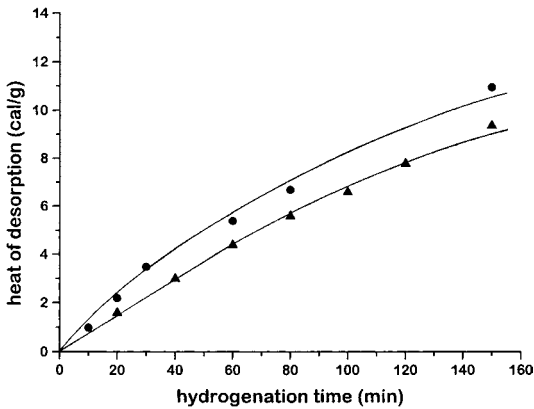


Fig. 4. Dependence of the heat of desorption on time of electrolytic hydrogen charging (●, Ni_{81.5}B_{18.5}; ▲, Fe₇₉B₁₄Si₇).

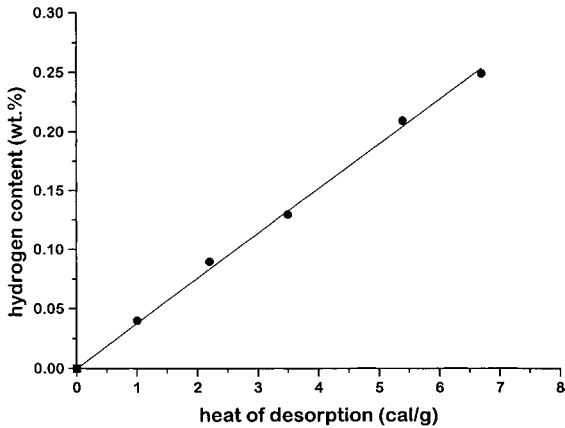


Fig. 5. Relation between the heat of desorption and the hydrogen content for Ni_{81.5}B_{18.5} amorphous alloy.

desorption (ΔH_{des} in cal/g alloy) determined at different hydrogenation times for the Ni–B alloy are larger in comparison to the values for the Fe–B–Si alloy, obviously due to the higher H-concentrations in the former amorphous alloy.

Fig. 5 shows the relation between the hydrogen content in the amorphous samples and the enthalpy change during the dehydrating reaction for the Ni–B alloy (summarized from Figs. 2 and 4); the values for the H-content at the corresponding enthalpy of hydrogen desorption are taken from the interpolation curve in Fig. 2. The linear dependence in Fig. 5 as well as the same temperature of dehydrating reveal that the hydrogen in all samples has a similar thermodynamic stability [10]. From the slope of the straight line, the

enthalpy of hydrogen desorption, 22 kJ/(mol H₂), related to the hydrogen amount in the alloy was determined. The largest ΔH_{des} -value determined after 150 min of hydrogenation (Fig. 4) is not included in Fig. 5, because it deviates substantially from linearity. We assume that this deviation from linearity is due to some interactions of the hydrogen with the alloy elements at higher H-concentrations, which is reflected in an increase of ΔH_{des} . It has to be mentioned, however, that hydrides were not detected by X-ray diffraction even at the highest hydrogen concentrations.

The enthalpy of H-desorption calculated in cal/(mol H₂) is higher for the Fe–B–Si alloy. This is probably connected with a higher activation energy for H-diffusion (respectively, lower hydrogen diffusivity) in amorphous Fe–B–Si than in amorphous Ni–B. This finding is in contrast to the results on the diffusion of hydrogen in crystalline α Fe and Fe-based alloys and Ni and Ni-based alloys, where it is well known that the activation energy for hydrogen diffusion is much higher for the Ni-based alloys [11]. The result obtained in the present study, however, is in good agreement with the study of Santos et al. [5], who found that the hydrogen diffusivity in the Fe-based amorphous alloys is much lower than in iron, while the difference between amorphous Ni₈₁P₁₉ and pure nickel is much smaller. Additionally, the presence of Si in Fe-based glasses is known to decrease the hydrogen diffusivity [12].

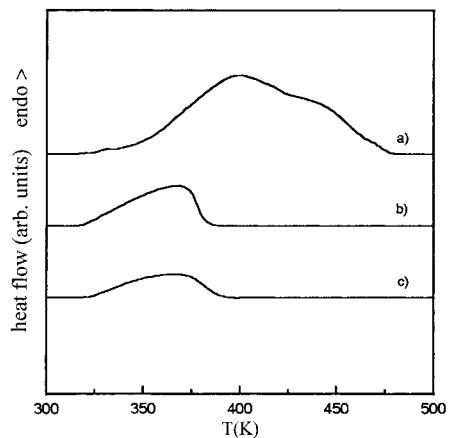


Fig. 6. DSC-traces of hydrogenated amorphous Ni–B after three different times of desorption at 300 K: (a) 0, (b) 30 and (c) 40 min.

Fig. 6 shows the DSC-traces of one hydrogenated Ni–B amorphous sample at three different times (0, 30 and 40 min) of desorption at ca. 300 K. These experiments have been carried out in order to compare the kinetics of hydrogen absorption and desorption. It was found that both the kinetics are comparable, with the desorption kinetics being slightly faster. After about one hour at 300 K, the hydrogenated sample is completely dehydrided.

4. Conclusion

The hydriding/dehydriding properties of amorphous $\text{Ni}_{81.5}\text{B}_{18.5}$ alloy were investigated from both the thermodynamic and kinetic aspect by DSC and thermogravimetry. The hydrogen content is saturated after hydrogenation times >4 h, finally reaching a value of ca. 0.40 wt.%. This value is higher than the maximum hydrogen content determined for an $\text{Fe}_{79}\text{B}_{14}\text{Si}_7$ amorphous alloy in a previous study under identical hydrogen charging conditions. The initial hydrogenation kinetics of both the glassy alloys were found to be comparable. Although the different hydrogen content, the dehydriding reaction for all Ni–B samples starts at ca. 350 K. A low-temperature endothermic DSC effect attributed to hydrogen desorption from the H-charged amorphous ribbons was observed (in the 350–450 K range), as the heat of H-desorption increases with the time of H-charging and reaches a value of ca. 11 cal/g alloy at 150 min of hydrogenation.

It was found that the enthalpy of hydrogen desorption for the Ni–B glass, 22 kJ/(mol H_2), is lower than

that obtained earlier for Fe–B–Si glasses which is in contrast with the results on hydrogen diffusion in crystalline iron and nickel. It is shown that hydrogen in the different samples (with different hydrogen content) has similar thermodynamic stability. Formation of hydrides was not detected. The kinetics of hydrogen absorption and desorption in Ni–B at ca. 300 K have been compared and it was found that the kinetics of desorption was slightly faster.

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