



Hydrogen-induced decomposition of Cu–Zr binary amorphous metallic alloys



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ABSTRACT

The hydrogen-induced phase separation of Cu–Zr binary amorphous alloys during hydrogen gas charging at elevated temperature was demonstrated; the homogeneous binary alloy was decomposed into pure Cu and Zr-hydride by absorbing hydrogen into the structure. The decomposition, which is attributed to the opposed affinity to hydrogen of Cu and Zr, took place in nanometer scale. The hydrogen absorption kinetics was compared for the alloys with different compositions. The structure after hydrogen absorption was analyzed using x-ray diffraction, ultra-small and small angle neutron scattering, and electron microscopy.

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1. Introduction

Atomic hydrogen is the smallest element and is likely to penetrate into metallic lattice. Inside metals, hydrogen sits in interstitial sites like other small elements (carbon, nitrogen, and oxygen) but has significantly higher mobility. For example, hydrogen in α -Iron [1] has a diffusivity several orders of magnitude higher than those of carbon [2], nitrogen [3] and oxygen [4]. Likewise, amorphous metals can absorb hydrogen and the diffusivity of hydrogen inside amorphous metals is comparable to those in other conventional crystalline metals [5]. Earlier studies on hydrogen in amorphous metals were made in search of effective solid-state hydrogen storage medium [6–8]. Recent interest has been shifted to the application as hydrogen permeable membranes [9,10]. For both applications, it is now generally accepted (at least for amorphous alloys) that the concentration of strong hydrogen attractor such as zirconium and titanium is the key factor determining the

properties; increase in zirconium content leads to (i) more hydrogen absorption for hydrogen storage [6] and (ii) more hydrogen flux through the amorphous ribbons for hydrogen permeable membranes [5,11,12]. However, zirconium content does not always work in favor of the properties; such increase facilitates the formation of either hydride or hydride-like short-range ordering thus resulting in an increased fraction of immobile trapped hydrogen in the total amount of absorbed hydrogen [13–15]. The trapping of hydrogen is not reversible; the trapped hydrogen can be liberated only by heating to a temperature high enough to cause crystallization of the hydrogen-bearing amorphous structure. In other words, to maintain the amorphous structure during service, the formation of stable hydrogen clusters has to be minimized.

On the other hand, such a structural change could be utilized for other purposes. For example, Ni–Zr binary amorphous alloys were exposed to oxidizing heat treatment to induce phase separation of the homogeneous amorphous structure resulting in metallic Ni and ZrO₂ composite structure which can be used as a catalyst for methanation reaction of H₂ and CO₂ [16]. The driving force for the phase separation was the difference in the affinity of Ni and Zr to oxygen; Zr preferentially forms oxide repulsing away Ni. For this

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catalysis application, each phase can be assumed to facilitate the adsorption of different molecules: metal for H_2 and oxide for CO_2 , and the key reaction must take place near the interface between the metal and the oxide. Therefore, minimizing the size of each phase is thought to be beneficial in enhancing the reaction rate, i.e., catalytic ability. However, no further study has been reported since Yamasaki and coworkers' work published in 2000 [16]; further development and optimization of the microstructure could have been made if there was a reliable way to control the structural change. Since Zr is a strong hydrogen attractor while Ni and Cu are not, hydrogen can also be used to induce the phase separation. And, as stated above, hydrogen can move much faster and deeper inside the metallic structure, which suggests hydrogen as a suitable candidate for this process.

Therefore, understanding the structural change of amorphous metals induced by hydrogen is crucial in designing and optimizing the alloys for the various applications previously described: hydrogen storage, hydrogen permeable membrane, and catalysis. In this context, this study infiltrated hydrogen into amorphous binary alloys, $Cu_{64}Zr_{36}$, $Cu_{56}Zr_{44}$, and $Cu_{50}Zr_{50}$, to investigate the structural change of the amorphous metallic structure caused by hydrogen absorption.

2. Experimental details

For this study, binary amorphous ribbons of Cu–Zr system ($Cu_{64}Zr_{36}$, $Cu_{56}Zr_{44}$ and $Cu_{50}Zr_{50}$) were prepared by a melt-spinning technique at Eco-FM Company (Incheon, Korea) with a width of 75 mm and a thickness of about 80 μm . Hydrogen charging was carried out inside a cylinder equipped with a pressure gauge by applying a hydrogen pressure of 8 bars for 24 h at the temperatures of 473, 573 and 673 K. According to a simple calculation based on the one-dimensional diffusion equation [15] using the hydrogen diffusivity and solubility of amorphous alloys [5], hydrogen penetration is so fast that hydrogen absorption is completed in less than 5 s for the entire 80 μm thick ribbons at 673 K. Differential scanning calorimetry (not shown in the present study) measured the glass transition (T_g) and crystallization (T_x) temperatures of the alloys. The measured values of $Cu_{64}Zr_{36}$ (T_g and T_x : 761 and 795 K, respectively), $Cu_{56}Zr_{44}$ (717 and 759 K), and $Cu_{50}Zr_{50}$ (694 and 737 K) were found to be consistent with the existing literature on thermal properties of Cu–Zr amorphous alloys [17–20]. For the alloy with the lowest T_g , $Cu_{50}Zr_{50}$ with 694 K, the highest treatment

temperature 673 K is about 21 K lower, which suggests that the alloys would not experience significant level of crystallization in the initial hour of heat treatment without hydrogen. However, with the fast diffusion of hydrogen, it is reasonable to assume that atoms in the alloys are already surrounded by the absorbed hydrogen while heating up to the treatment temperature. As absorbed hydrogen has been reported to alter the thermal stability of amorphous structure [21,22], the alloys with hydrogen are expected to show structural change by the cooperative work of hydrogen and temperature, therefore not solely by the temperature.

A piece of 200 mg for each composition was mechanically polished with silicon carbide paper prior to charging, in order to remove any surface oxide layer. No additional surface treatment was performed before the hydrogen charging because the charging time was long enough to ensure sufficient hydrogen diffusion into the whole structure, even under sluggish surface kinetics for the dissociation of hydrogen molecules into hydrogen atoms which is a necessary step for the hydrogen absorption of any metallic structure. To reveal the microstructural change induced by hydrogen absorption, X-ray Diffraction (XRD, Dmax 2500/DC, Rigaku, Japan), Scanning Electron Microscopy (SEM, Inspect F, FEI, Netherland), Transmission Electron Microscopy (TEM, Tecnai F20, FEI, Netherland), Ultra Small Angle Neutron Scattering (KIST-USANS, HANARO Cold Neutron Facility, Korea) and Small Angle Neutron Scattering (18m-SANS, HANARO Cold Neutron Facility, Korea) were utilized.

3. Results and discussions

Fig. 1 shows the hydrogen absorption kinetics of the three different compositions. Hydrogen charging resulted for all specimens in a severe drop of the applied pressure describing hydrogen penetration into the alloys. For most compositions, hydrogen absorption proceeds with fast kinetics within 3 h, during which the absorbed amount increases dramatically before saturation. Both absorbed amounts and kinetics of hydrogen diffusion increased along with the increase in zirconium concentration as well as temperature. Therefore, $Cu_{50}Zr_{50}$ specimens treated at 573 and 673 K displayed the maximum hydrogen absorption (about 1.08 and 1.14% wt).

Fig. 2(a) shows XRD patterns of $Cu_{50}Zr_{50}$ after hydrogen charging for 24 h at 473, 573 and 673 K. The as-received sample shows only a broad hump indicating that it is amorphous, whereas

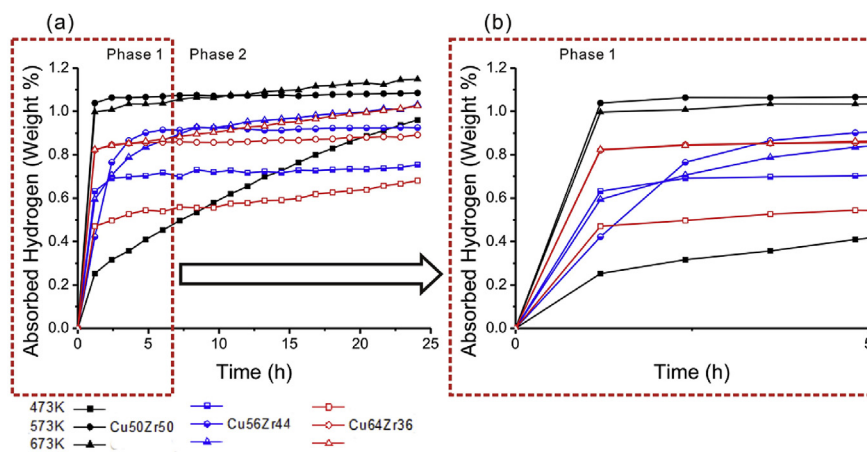


Fig. 1. (a) Absorbed amount of atomic Hydrogen (weight %) during charging process plotted with charging time for the three alloys: $Cu_{50}Zr_{50}$, $Cu_{56}Zr_{44}$, and $Cu_{64}Zr_{36}$, and three different charging temperatures: 473, 573, and 673 K. (b) Magnified plot of (a) displaying the area marked by the dotted square in (a) to show the early stage absorption behavior during the first 5 h of charging.

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