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## New insights into melt hydrogenation effects on glass-forming ability in a Zr-based bulk metallic glass

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## ABSTRACT

Notable improvements in the glass-forming ability (GFA) of Zr-based metallic glasses with melt hydrogenation have been reported in our previous studies. The effects of hydrogen on GFA are usually explained via short-range structural order, local symmetry, structural free-volume, and bonding character. To fundamentally understand why hydrogen enhances GFA, thermal analyses were carried out on a  $Zr_{55}Cu_{30}Ni_5Al_{10}$  amorphous alloy to assess how hydrogen affected viscosity, fragility, critical cooling rate, and Gibbs free energy difference,  $\Delta G$ . Amorphous alloys subjected to melt hydrogenation were found to possess higher viscosity and lower fragility, indicating increased GFA. The critical cooling rate of hydrogenated alloy melts gradually decreased and the lowest critical cooling rate was 10 K/s when the alloy was fabricated in Ar + 10% $H_2$ . The liquid/solid  $\Delta G$  of melt-hydrogenated alloy was significantly smaller than that of the equivalent non-hydrogen alloy. From thermodynamic and dynamic perspectives, viscosity, fragility, critical cooling rate, and  $\Delta G$  demonstrated that melt hydrogenation improved these alloys' GFA and explained the present experimentally observed improvements in GFA.

## 1. Introduction

Bulk metallic glasses (BMGs) possess important qualities for applications in engineering and structural materials, which include superior mechanical properties, such as high strength and hardness and good corrosion resistance [1–5]. BMGs are well known to often possess limited glass-forming ability (GFA) and poor room-temperature plasticity, which restricts potential applications as structural materials [6–8]. Investigations into a wide variety of binary and multicomponent alloys have focused on the formation, structures, and properties of metallic glasses [9–18]. Critical factors, in terms of GFA and mechanical properties, include the nature and number of components and the purity of constituent elements [19–22]. A material's composition greatly affects on the GFA and properties of BMGs. Thus, glass formation, thermal stability, and various properties of BMGs are greatly influenced by minor alloy additions. Thermodynamic, dynamic, GFA, mechanical, and physical properties of amorphous alloys can be effectively tuned and improved by minor additions of metalloid, metallic, or rare earth elements. As a result of this understanding and the desire to enhance the GFA of BMGs, strategies for alloy design have focused on

microalloying, which involves the addition of small amounts of suitable elements.

The formation process of amorphous alloys refers to a process in which crystal nuclei formation is avoided while an alloy melt cools. The formation of amorphous alloys is closely related to the alloy's structure, thermodynamics, and dynamics [23–25]. From a structural point of view, a more stable, disordered, and effective solid accumulation is formed between large and small atoms as a result of differences in structural dimensions among multiple components of bulk amorphous alloys. The area of an alloy's solid/liquid interface can be increased in such a structure, thus making the crystal nucleation process more difficult. Meanwhile, the structure sharply increases the alloy melt's viscosity during the supercooling process, thus making atomic diffusion difficult in the supercooled melt, inhibiting nucleation and growth of crystal phases. In terms of thermodynamics, for an alloy system to attain strong amorphous GFA, the systemic Gibbs free energy difference  $\Delta G$ , in which a melt transforms to crystal phases, should be minimized. A multiple component system increases the entropy change of bulk amorphous alloys during the crystal formation process. Differences in atomic size among various components decrease the system's enthalpy

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change, reduce the systemic  $\Delta G$ , and strengthen the GFA of an amorphous alloy. In term of dynamics, alloy melts can form amorphous alloys when they effectively inhibit formation and growth of crystal phases in the melt during solidification. Decreased homogeneous nucleation and crystal growth rates in a supercooled liquid melt leads to strengthened GFA.

As the presence of gaseous elements is detrimental to BMG production, stringent protective conditions are required. Although a vacuumization process is usually involved to remove gases, relatively few studies of BMGs and the effects of gaseous element composition have been performed. Recently, in certain alloy systems, microalloying with oxygen or nitrogen has been shown to improve the GFA [15,20,26], implying that BMG's GFA is greatly influenced by certain gaseous elements. As hydrogen possesses the smallest nonmetal atomic radius, it would be logical to predict that it could have significant effects on GFA, but few studies have focused on these effects. In recent studies, hydrogen has been investigated as an alloying element in metallic glasses. In the present study, the method for hydrogen addition was novel, using a gas-phase processing route to introduce hydrogen. Also, the GFA of Zr-based BMGs has been improved by minor hydrogen doping [27–29]. Although many studies have reported the above phenomena, it is noteworthy that few studies have focused on the formation mechanism of the resulting amorphous alloy.

Based on previous research, liquid hydrogenation has been found to be able to strengthen the GFA of amorphous alloys [30]. In this paper, the effects of hydrogen addition on amorphous alloy's GFA were discussed from thermodynamic and dynamic perspectives. Providing valuable insights into the mechanism of GFA in BMGs, the results presented here can serve as a basis for the development of future techniques for enhanced BMG performance.

## 2. Experimental

The raw materials used for preparation of amorphous alloys were high-purity metals, > 99.9% pure (wt%), including Zr, Cu, Ni, and Al. An alloy composition of  $Zr_{55}Cu_{30}Ni_5Al_{10}$  (at%) was chosen for this study. The raw materials were placed in a water-cooled copper hearth, which was then flushed with a hydrogen-argon gaseous mixture with set partial pressures. The hydrogen proportion in the mixed gases was controlled by a JF-2200 hydrogen analyzer. The metal mixtures were first melted together into master alloys using an electric arc furnace with a tungsten electrode and  $60 \times 15 \times 3$  mm samples prepared using a copper-mold suction-casting method. A series of hydrogen-containing alloys were prepared in this fashion with varying amounts of hydrogen in the Ar/H<sub>2</sub> gas mixture. The alloy hydrogen content was used in labels to denote the gas mixture used during preparation, i.e., Ar, Ar + 5%H<sub>2</sub>, Ar + 10%H<sub>2</sub>, Ar + 15%H<sub>2</sub>, and Ar + 20%H<sub>2</sub> alloys. The gas mixture was entirely hydrogen/argon.

A sample's phase structure was determined using with a Rigaku D/max-rB X-ray diffractometer (Rigaku Corp., Tokyo, Japan) and subjected to Cu-K $\alpha$  radiation, with a scanning speed of 5°/min and diffraction angle range of 20–100°. The hydrogen and oxygen sample contents were determined using a Leco ROH600 oxygen-hydrogen analyzer (Leco Corp., St. Joseph, MI, USA). This was accomplished by melting a portion of each sample under a protective layer of helium, during which the sample's trapped oxygen and hydrogen were released and entered the analyzer's infrared detection cell. Differential scanning calorimetry (DSC) studies were performed at a constant heating rate of 0.333 K/s. The hydrogen content  $C_H$ , thermal parameters, and critical section sizes  $Z_c$  of the prepared alloys under Ar + x%H<sub>2</sub> atmospheres are shown in Table 1 [30]. For a special hydrogenated metallic glass, DSC measurements were also performed at different rates, from 0.167 to 2.667 K/s, for derivation of the uncooled liquid's fragility parameter.

## 3. Results and discussion

### 3.1. Effects of liquid phase hydrogenation on Supercooled melt viscosity

The question of how some alloy systems, with very strong GFA, can form large-sized metallic glass under a low cooling speed was addressed here. Actually, the process by which a supercooled liquid forms an amorphous alloy is a process that inhibits the formation and growth of crystal phases. As nucleation and growth are jointly determined by thermodynamic and dynamic factors, it was particularly important to study these factors in the present  $Zr_{55}Cu_{30}Ni_5Al_{10}$  alloys after melt hydrogenation.

Based on classic nucleation theory, the nucleation and growth rates should be controlled as much as possible to obtain large-sized metallic glasses. The equation for the nucleation and growth rates in classic nucleation theory are expressed as:

$$I = \frac{A_v}{\eta} \exp\left(-\frac{16\pi\sigma^3}{3k_B T \Delta G_{l-s}^2}\right) \quad (1)$$

$$u = \frac{k_B T}{3\pi a_0^2 \eta} \left[1 - \exp\left(-\frac{n\Delta G_{l-s}}{k_B T}\right)\right] \quad (2)$$

where  $A_v$  is the kinetic constant during nucleation,  $k_B$  the Boltzmann constant,  $\eta$  the viscosity function of the supercooled liquid changing with temperature,  $\sigma$  the solid-liquid surface energy,  $\Delta G_{l-s}$  the  $\Delta G$  between the supercooled liquid and crystalline state,  $a_0$  the average atomic diameter,  $n$  the average atomic volume, and  $T$  the absolute temperature.

Based on the above equation from classic nucleation theory, the viscosity coefficient is one of the critical factors influencing nucleation and growth of crystal phases. The atomic migration ability of the melt is embodied in the viscosity and is an important factor that reflects the binding force between atoms and atomic transport properties. The microstructure of an alloy melt is also directly associated with the viscosity coefficient [31]. Under the action of kinetic viscous effects, a supercooled alloy melt will avoid nucleation and growth, forming an amorphous structure. Therefore, the viscosity magnitude is closely associated with the alloy's GFA. In nonequilibrium solidification theory, when the critical cooling rate is high enough, it is believed that the liquid's viscosity coefficient increases and atomic migration rate decreases, thus avoiding structural relaxation. As the temperature continues to decline, the material maintains a nonequilibrium state and glass transition occurs, indicating that the viscosity magnitude plays a significant role in inhibiting nucleation and growth of crystal phases. Turnbull has calculated the viscosity variation of amorphous alloys with temperature using the following equation [32]:

$$\eta = 10^{-3.3} \exp\left(\frac{3.34T_m}{T - T_g}\right) \quad (3)$$

where  $\eta$  is the viscosity,  $T_m$  the alloy melting point, and  $T_g$  the glass transition temperature.

Based on Eq. (3), the viscosity variation with temperature in the supercooled liquid phase region was observed in  $Zr_{55}Cu_{30}Ni_5Al_{10}$  alloys prepared in mixed Ar/H<sub>2</sub> atmospheres at different ratios (Fig. 1). The viscosities of Ar, Ar + 5%H<sub>2</sub>, and Ar + 10%H<sub>2</sub> alloys exhibited an increasing trend with decreased temperature. Alloy viscosities prepared in an Ar/H<sub>2</sub> atmosphere were significantly higher than that of the Ar alloy. H<sub>2</sub> addition clearly increased the viscosity of the alloy melt, which indicated that H<sub>2</sub> addition increased the alloy's interatomic friction forces and made interatomic structural reorganization difficult, thus inhibiting crystal generation and improving the alloys' GFA.

### 3.2. Effects of melt hydrogenation on the fragility parameter

In 1985, Angell proposed the concept of supercooled liquid fragility

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