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The mechanism of hydrogen-induced amorphization in intermetallic compounds

Yong-Gyoo Kim and Jai-Young Lee
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Kusong-Dong 373-1, Yusung-Ku, Taejon (South Korea)

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Abstract

In this article, the amorphization mechanisms of intermetallic compounds by hydrogen absorption are discussed on the basis of reported experimental results. It is found that there are two different modes for amorphization. One is a gradual and thermally activated process, while the other is a strain-induced reaction during hydrogen absorption. As factors affecting the amorphization modes, the hydrogen concentration and the elastic property of the compound are discussed. Of these two factors the elastic property of the compound plays a key role on the amorphization. When an elastic strain exceeding the elastic limit was imposed on the compound, the crystal lattice was not deformed plastically but collapsed into the amorphous state because the brittleness of the compound did not permit plastic deformation.

1. Introduction

It has been found that amorphous alloys can be prepared by the solid state reaction [1]. As an example of the compounds obtained by these new methods, some intermetallic compounds have been found to lose their crystallinity by hydrogen absorption at ambient conditions. The first discovery was made by Yeh *et al.* [2] on the $L1_2$-type Zr_3Rh system. After this discovery, many alloy systems including RM_2 (R ≡ rare earth; M ≡ transition elements) Laves phases were reported to transform to an amorphous state by hydrogen absorption [3–5]. Although many empirical results on hydrogen-induced amorphization have been reported, very little is understood about the underlying mechanism.

In previous work, it was found that there are two different modes for the amorphization of the compounds [6]: one is the gradual crystal-to-amorphous transition from the crystalline hydride state (mode I), and the other is the direct reaction during the hydrogen absorption process (mode II). It was explained as a concept of the glass expansion gap, which depends on the elastic modulus of the compound. However, the differences between the mechanisms of these two modes have not been discussed clearly.

In this article, the amorphization mechanism of intermetallic compounds obtained by hydrogen absorption will be discussed on the basis of reported experimental results, including our unpublished work.

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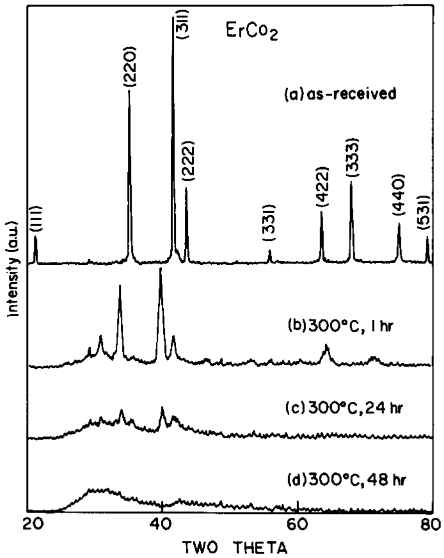
2. Discussion on the amorphization mechanism

As an example of mode I, Fig. 1 shows the X-ray diffraction (XRD) patterns of the $ErCo_2$ phase, which is a C15 Laves phase with $a = 7.154$ Å, for various reaction times when hydrogenated at 300 °C under an H_2 pressure of 50 atm. Initially, hydrogen absorption induces an isotropic volume expansion of the lattice. As the reaction time increases, the Bragg peaks corresponding to the crystalline $ErCo_2H_x$ phase disappear gradually, and finally the compound transforms to an amorphous state after 48 h, which was confirmed by the electron diffraction pattern. This amorphization reaction becomes faster as the reaction temperature increases, which indicates a thermally activated process. From a kinetic study on the amorphization of the $ErNi_2$ system [7], which has the same crystal structure and same amorphization process as the $ErCo_2$ phase, an activation energy of 17 kcal mol^{-1} is obtained and explained as due to the motion of the smaller metal atoms (nickel) within a very short range. The driving force for the reaction is accepted as the difference between the free energies of the hydrogen occupation sites in the crystalline and amorphous state so that the surroundings of the hydrogen atoms in the amorphous state resemble those of hydrogen atoms in the crystalline ErH_2 phase [8].

In Fig. 2, the XRD patterns of the $CeFe_2$ phase, which is a C15 Laves phase with $a = 7.303$ Å, before and after hydrogenation at 50 atm are shown. Because of hydrogen absorption, no crystalline reflections are seen at any



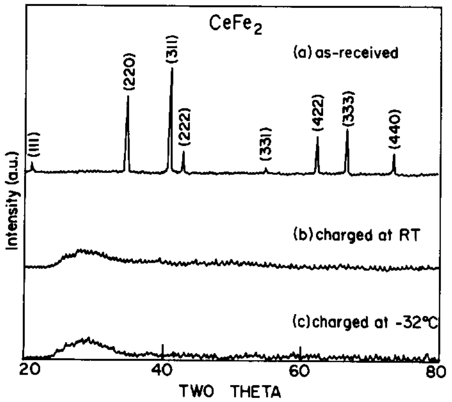


Fig. 1. XRD patterns of $ErCo_2$ for various reaction times when hydrogenated at 300 °C and an H_2 pressure of 50 atm.

Fig. 2. XRD patterns of the $CeFe_2$ before and after hydrogenation at various charging temperatures at an H_2 pressure of 50 atm.

charging temperatures. Transmission electron microscopy investigation verified that the hydrogenated $CeFe_2H_x$ phase was truly amorphous. Furthermore, the $CeNi_2$ phase, which has the same crystal structure as $CeFe_2$, can lose its crystallinity as a result of hydrogen absorption, even at a lower temperature such as −76 °C [9]. These compounds can be treated as representative systems of mode II. At low temperatures such as −76 °C, the mobility of metal atoms should be extremely small and thus lead to hardly any diffusional transformation through the vibrational mode of metal atoms. However, the hydrogenation treatment can induce amorphization as shown in Fig. 2. In order words, an athermal reaction such as the martensitic transformation takes place. This type of reaction does not need thermal energy to overcome the activation energy barrier for the transformation.

It is obvious that each amorphization mode is clearly different from the viewpoint of the energy criteria of thermal energy and elastic energy. It may be controlled by the mutual competition between the two major factors of thermal energy and elastic energy. In this paper, the following are considered as factors affecting the amorphization mode: (i) hydrogen concentration; (ii) thermodynamic and elastic properties of the compound.

Let us consider the effects of hydrogen concentration on the amorphization. Hydrogen atoms located at the interstitial sites would apply a large elastic stress to the lattice and supply chemical mobility for the motion of metal atoms due to the interaction between the hydrogen-absorbing element and the hydrogen atom. The chemical mobility represents the driving force for the phase separation such that all RM_2 ($R \equiv$ rare earths; $M \equiv$ transition elements) Laves phases and other zirconium-based compounds are decomposed into binary hydrides and other compounds or elemental phases as the final equilibrium state [2–5, 10]. When confined to RM_2 Laves systems, the rare earth elements R have a similar chemical affinity to hydrogen or heat of formation as the binary hydride. The transition elements M have a much smaller hydrogen affinity than rare earths and there is a very small difference between them [11]. Thus it is believed that the chemical mobility may be nearly the same regardless of the alloy system if the final products are RH_2 + elemental M. Therefore, as discussed above, the distinct difference in amorphization modes is not definitely related to the chemical affinity between the constituents and hydrogen atoms.

Hydrogen atoms located in the matrix can be treated as point defects, and they will impose an elastic stress on the material. Thus the hydrogen concentration in the compounds may change the amorphization behaviour greatly. In fact, DyM_2 ($M \equiv$ Mn, Fe, Co, Ni) Laves phases were reported to transform into an amorphous state at 25 °C under an H_2 pressure of 150 atm, even though lattice expansions occur only at 1 atm at 25 °C [12]. At high hydrogen pressures the amorphization behaviour follows mode II, but mode I at low pressures. This indicates that the amorphization mode changes with the hydrogen pressure, *i.e.* the hydrogen concentration. However, the absolute value of hydrogen concentration cannot be a measure of the amorphization mode. The $ErCo_2$ phase, which undergoes the mode I process, can absorb hydrogen up to [H]/[M] = 3.67, giving $ErCo_2H_{3.67}$, at room temperature and an H_2 pressure 50 atm. On the contrary, the $CeFe_2$ phase, with a mode II process, absorbs hydrogen up to [H]/[M] = 3.0 at 20 °C and 5 MPa [13]. In spite of the smaller hydrogen concentration of the latter under similar conditions, it follows the athermal reaction process. Therefore, from these results, it is suggested that the amorphization mode may be controlled by the relative strength of elastic strain that the material may feel, even though the mode is related to the hydrogen concentration in the same alloy system.

Next we consider the effects of properties of the compound itself. The properties of the compound are classified into two major aspects: thermodynamic and elastic properties. The thermodynamic properties are related to the bonding force of the compound or compound stability, and therefore the decomposition temperature or formation enthalpy can be a measure of this. The elastic properties can be related to the degree of expansion during hydrogen absorption, and thus the elastic modulus value is the direct measure.

In the case of higher compound stability or larger bonding force, a higher thermal energy is needed for the material to break and rearrange for amorphization. Thus a compound with a high decomposition temperature or a large negative heat of formation can be amorphized at high reaction temperatures. In previous work [6], it was shown that RM_2 ($M \equiv Fe$, Ni) Laves phases follow a mode I process as the heat of formation becomes more negative, but the absolute value is not a measure of the amorphization mode. Only a relative comparison for alloy systems with the same transition element is possible.

The next concern is the relation between the amorphization mode and the elastic modulus. The elastic modulus is the ratio of applied stress to strain, and there are also the bulk modulus, Young's modulus and shear modulus to consider. Hydrogen absorption in the intermetallic compounds leads to uniform lattice expansion throughout the three axes except for some compounds such as FeTi [14] or $ErNi_2$ [7]. When the hydrogen atoms as a point defect apply an isotropic elastic stress in the lattice, the degree of elastic strain (volume expansion) depends on the bulk modulus of the compound. Previously, we used Young's modulus as the parameter of lattice expansion in Laves phases [6]. Fortunately, there is no critical problem about the discussion because Young's modulus and the bulk modulus of the rare earth elements have the same trend with increasing atomic number. As the atomic number of rare earths increases, these moduli increase similarly.

As the elastic modulus becomes larger, the degree of deformation on applied stress becomes smaller. In other words, at the same hydrogen concentration, the volume expansion of the compound can be determined by the elastic modulus, especially the bulk modulus. A compound such as the $CeFe_2$ system shown in Fig. 2 with a small bulk modulus may be easily expanded. Moreover, hydrogen absorption in cerium-based compounds gives a much larger expansion than in other rare earth compounds because the valence state of cerium is changed from 4+ in the metallic state to 3+ in the hydrided state [15, 16]. However, because the $CeRu_2$ phase has a higher elastic modulus than the $CeFe_2$ or $CeNi_2$ system, it forms a crystalline hydride phase when hydrogenated at room temperature and an H_2 pressure of 50 atm [17], even though an abnormally large volume expansion of about 37 vol.% occurs.

Owing to the elastic strain created by the hydrogen absorption, most of the compound is disintegrated into fine particles, but the major portion of strain is accumulated on the matrix, resulting in lattice expansion. Thus the fact that the crystalline hydride phase is observed arises because it is possible for the material to accommodate the elastic strain. However, if the elastic stress exceeds the elastic limit, the material cannot preserve its original state any more. In other words, plastic deformation should take place, but the brittleness of the intermetallic compound does not permit sufficient plastic deformation and, because this deformation is impossible, the disintegration of particles proceeds as a type of dissipation of elastic strain. Hydrogen absorption takes place uniformly within the whole crystal matrix. If the elastic strain were released only by fragmentation, the material would be broken into a unit lattice of the crystal. However, this is impossible and has not been reported anywhere. Instead of disintegration of the matrix, it is suggested that collapse of the crystal lattice occurs as a type of plastic deformation. This collapse can release the strain and lower the total free energy of the system. This phenomenon is exactly an amorphization process. An elastic strain which the compound cannot accommodate causes the disordering of the lattice into a more stable amorphous state. The reaction process is controlled by the hydrogen absorption rate into the system.

Cahn and Johnson [18] proposed that the amorphization processes by solid state reaction resembled the ordinary melting process. Okamoto *et al.* [19] suggested that the amorphization of Zr_3Al compound by ion irradiation was triggered by the elastic instability. The above discussions concern the decrease in the elastic modulus during amorphization, and the crystal structure cannot be maintained when the elastic modulus falls below a critical value. Many researchers have pointed out the importance of the elastic strain, *i.e.* the build-up of lattice defects, on solid state amorphization [20–22]. Thus it is proposed that the $CeRu_2$ or $ErCo_2$ phases, which do not exhibit amorphization phenomena in the low temperature range, can be amorphized at more severe charging conditions. Further work is needed to confirm this suggestion.

3. Summary

It is concluded that the amorphization modes of the intermetallic compounds by hydrogen absorption have clearly different natures of transformation for various compounds. One is a thermally activated process (mode I), and the other is an athermal reaction (mode II). The driving force and the mechanism for the reaction are the free-energy decrease through the phase

TABLE 1

Classification of the two different amorphization modes

Mode	Reaction	Example of system	Process	Mechanism	Driving force	Elastic modulus	Decomposition temperature	Heat of formation
Mode I	$c\text{-}RM_2 + H_2$ $\rightarrow c\text{-}RM_2H_x$ $\rightarrow a\text{-}RM_2H_x$	$ErCo_2$	Thermally activated	Motion of metal atoms	Phase decomposition	High	High	High
Mode II	$c\text{-}RM_2H_x$ $\rightarrow a\text{-}RM_2H_x$	$CeFe_2$	Athermal	Hydrogen absorption	Strain release	Low	Low	Low

c-, crystalline; a-, amorphous.

The elastic modulus, decomposition temperature and heat of formation are given as a relative comparison for each mode. The values for the heat of formation provide a comparison in absolute value for modes I and II.

separation and the short-range motion of transition metals for mode I and correspond to the release of the elastic strain energy and hydrogen absorption for mode II. The general features of the two different modes are summarized in Table 1.

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