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Absorption of hydrogen in Zr based amorphous alloys under high pressures of gaseous hydrogen

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Abstract

Amorphous and crystalline $Ni_{91}Zr_9$, and $Cu_{50}Zr_{50}$ were exposed to gaseous hydrogen at pressures exceeding 1 GPa(H_2). The in situ measurements of relative electrical resistance and thermoelectric power as a function of hydrogen pressure were carried out for amorphous and crystalline $Ni_{91}Zr_9$ samples. Similar measurements were not possible for $Cu_{50}Zr_{50}$ alloys due to their brittleness caused by the hydrogen uptake. The change of electrical resistance for crystalline bcc $Ni_{91}Zr_9$ samples clearly indicated the transformation into the hydride phase at hydrogen pressure near 0.67 GPa(H_2). The behaviour of the amorphous $Ni_{91}Zr_9$ was different showing a continuous character of hydrogen absorption and desorption. The hydrogen absorption slightly reduced the initial positive value of thermoelectric power of both crystalline and amorphous alloys according to the general tendency observed for nickel alloyed with transition elements belonging to the left half of the transition group. The values of hydrogen concentration in the alloys exposed to the high hydrogen pressure are given. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Amorphous alloys; Hydrogen absorption; High hydrogen pressure

1. Introduction

Application of the high hydrogen pressure techniques in the research of the metal–hydrogen systems resulted in synthesis of new crystalline hydrides and highly hydrogenated amorphous alloys [1–3]. The high-pressure technique, offering a very large range of exactly determined hydrogen activities (chemical potentials), is especially useful in investigating metal–hydrogen systems that cannot be obtained by any other method or are metastable (like nickel rich alloys, including the $Ni_{91}Zr_9$ alloy) at normal conditions.

The $Ni_{91}Zr_9$ and $Zr_{50}Cu_{50}$ alloys, studied in this work, belong to a relatively small group of alloys, which can be prepared in both one-phase crystalline and amorphous modifications. Therefore, their investigation can provide us with a better understanding of the role of structural factors in the phenomena related to hydrogen absorption and desorption.

2. Experimental

The $Cu_{50}Zr_{50}$ crystalline alloy was obtained as a one-phase material by the arc melting process. The $Ni_{91}Zr_9$ and $Zr_{50}Cu_{50}$ amorphous alloys were prepared by the conventional melt spinning method. In order to obtain the crystalline $Ni_{91}Zr_9$ alloy a special procedure was necessary, as the solubility of zirconium in the fcc phase of nickel is very limited. Therefore the $Ni_{91}Zr_9$ was melt spun at the cooling rate (smaller than that necessary to obtain amorphous alloy) appropriate to receive one-phase bcc crystalline alloy. The lattice parameter of this alloy has been determined as $a=0.2851$ nm.

The electrical resistance and thermoelectric power were measured in situ under high pressure conditions by using a device described elsewhere [1]. The temperature of the high pressure apparatus has been kept constant by using a temperature control system. The values of the hydrogen absorption were determined by mass spectrometry.

3. Results and discussion

3.1. The $Ni_{91}Zr_9$ alloys

The change of the relative electrical resistance as a function of hydrogen pressure for the $Ni_{91}Zr_9$ crystalline

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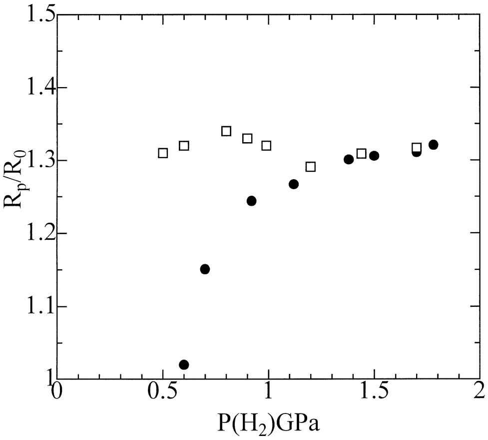

Fig. 1. The relative electric resistance R_p/R_0 of crystalline bcc $Ni_{91}Zr_9$ samples as a function of hydrogen pressure at 25°C (● pressure increase; □ pressure reduction). R_0-resistance at normal pressure. R_p-resistance in the equilibrium conditions with hydrogen at pressure P.

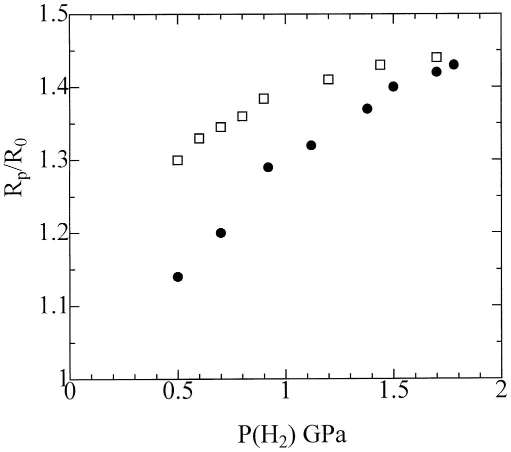

Fig. 2. The relative electric resistance R_p/R_0 of amorphous $Ni_{91}Zr_9$ sample as a function of hydrogen pressure at 25°C (● pressure increase; □ pressure reduction). R_0-resistance at normal pressure. R_p-resistance in the equilibrium conditions with hydrogen at pressure P.

alloy (Fig. 1) has behaviour typical for nickel doped with a transition metal [1]. The sharp resistance increase (about 30% of the initial, i.e. without hydrogen, value), indicating the hydride formation, takes place near 0.67 GPa(H_2) thus at the pressure slightly higher than in the case of pure nickel [1,4]. After formation of hydride the curve becomes flat reflecting the fact that the hydrogen absorption in the hydride phase is very small.

During the pressure reduction desorption and absorption curves initially do not differ. However, when the pressure is reduced below the hydride formation value a large hysteresis is observed. As in the case of pure nickel the decomposition of the $Ni_{91}Zr_9$ hydride takes place at a pressure several kbars lower than the pressure of the hydride formation. The hydrogen concentration as well as the resistance increment reached higher values than during the hydrogenation of these alloys by electrochemical means [5].

The zirconium affinity towards hydrogen is much higher than that of pure nickel. In spite of this the substitution of nickel by zirconium results in a remarkable shift of the hydride phase formation towards higher pressures (higher chemical potential of hydrogen). Similar behaviour was found also for the nickel-vanadium alloys for which the hydride formation pressure rises markedly with increasing concentration of vanadium [6].

The amorphous $Ni_{91}Zr_9$ sample behaved differently from its crystalline counterpart. This reflects the difference in the process of hydrogen absorption related to the structural differences. During the pressure increase no step-like changes or plateaus were observed for the amorphous sample. The change of the electrical resistance as a function of hydrogen pressure for both absorption and desorption branches was monotonic and continuous (Fig. 2). This behaviour is typical for amorphous alloys–hydrogen systems [7]. The large absorption/desorption hysteresis has been observed also for the amorphous alloy.

The thermoelectric power for both, the crystalline and amorphous samples in the hydrogen-free states, was positive giving the values +5.6 μV/K and +8.4 μV/K, respectively. The positive thermoelectric power of nickel alloyed with the metal belonging to the left half of transitional series was attributed to the presence of the virtual bound state in the vicinity of the Fermi level [8]. For such alloys, at some concentration range of alloying element the transformation into the hydride phase can occur without (or with only a small) change of the thermoelectric power [9]. This was revealed also for $Ni_{91}Zr_9$ alloys investigated here. For both, crystalline and amorphous $Ni_{91}Zr_9$ alloys the thermoelectric power decreased gradually with increasing hydrogen pressure. At the hydride phase formation the change of thermoelectric power of the crystalline alloy was smaller than 1 μV/K.

The hydrogen content in samples saturated at 0.7 GPa and 25°C was 0.52 H/Me and 0.39 H/Me for crystalline and amorphous alloys respectively. These values are smaller than the maximal value expected, especially for the amorphous alloy. However, the higher concentrations can be obtained at higher hydrogen pressures.

At normal conditions the hydrogenated phases were unstable; they released hydrogen continuously for several hours.

3.2. The Zr–Cu alloys

The determination of hydrogen influence on the electrical properties of $Zr_{50}Cu_{50}$ alloys (both crystalline and amorphous) was not possible since this alloy was extremely brittle in a hydrogen atmosphere. After the hydrogen uptake (even as small as 0.2 H/Me) the samples usually broke in several pieces making the measurement of their electrical resistance or thermoelectric power impossible. The kinetics of hydrogen absorption at 25°C was very slow; after 200 h long exposure at $p(H_2)=1.1$ GPa the hydrogen concentration (determined as hydrogen to metal ratio) was as low as 0.06 and did not change even after 3 month long exposure at the same pressure conditions. The increase of pressure up to 2.7 GPa(H_2) resulted in the value of 0.07 after 100 h of exposure. The possible reason for such a small absorption rate could be the presence of the copper enriched layer at the surface of the alloy. Copper does not form hydride in a direct reaction with hydrogen and is not penetrable to the hydrogen gas. Therefore the copper-enriched layer can play the role of a barrier responsible for the retardation of the hydrogen absorption process [10].

Increasing temperature up to 100°C resulted in a remarkable enhancement of the hydrogen absorption. After 75 h long exposure at pressures 1.0 GPa(H_2) and 1.1 GPa(H_2) the hydrogen contents in the amorphous $Zr_{50}Cu_{50}$ alloy, expressed in the H/ZrCu atomic ratio, were 1.2 and 1.4 respectively which suggests that copper also plays an active role in the hydrogen absorption in this amorphous alloy.

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