Nonequilibrium Crystalline and Amorphous Zr-Zn Alloys Produced by Vapor Quenching

By Hideyuki Yasuda*, Kenji Sumiyama** and Yoji Nakamura**

X-ray diffraction, differential scanning calorimetry (DSC), magnetization and electrical resistivity were measured for Zr_xZn_{1-x} alloys produced by vapor quenching. An amorphous phase was obtained for $0.2 < x < 0.7$, while a single hcp phase for $x < 0.1$ and $x > 0.75$. The crystallization temperature increases from 520 to 830 K with increasing x . The amorphous Zr_xZn_{1-x} alloys with $x = 0.3-0.4$ are paramagnetic even at 4.2 K, in contrast to the ferromagnetism in the Laves phase $ZrZn_2$ at low temperatures. The residual resistivities of these vapor quenched Zr_xZn_{1-x} alloys are higher than $1 \mu\Omega m$. The temperature coefficient of resistivity of the amorphous phase is negative between 4.2 and 270 K.

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I. Introduction

Vapor quenching techniques, such as sputter-deposition and thermal evaporation, are known to be capable of producing a wider variety of nonequilibrium alloys than the ordinary liquid quenching techniques⁽¹⁾. In vapor quenched alloys, amorphous alloys are often obtained in the concentration range involving intermetallic compounds in their equilibrium phase diagrams⁽²⁾⁻⁽⁴⁾. Since Zr and Zn form various intermetallic compounds, $ZrZn_{14}$, $ZrZn_6$, $ZrZn_3$, $ZrZn_2$ and $ZrZn$, in the equilibrium phase diagram⁽⁵⁾, an amorphous phase is expected to be formed in vapor quenched Zr-Zn alloys. However, the fabrication of Zr-Zn alloys by usual melting or liquid quenching is extremely difficult because of a large difference between the melting points of Zr, 2125 K and Zn, 693 K.

Among these intermetallic compounds, the C15 type Laves phase $ZrZn_2$ produced by sintering shows a typical weak itinerant electron ferromagnetism⁽⁶⁾⁽⁷⁾. Since the ferromagnetic property is sensitive to chemical

disordering⁽⁸⁾, it is interesting to study the effect of chemical disordering on the magnetic property of Zr-Zn alloys.

In this paper, we report the experimental results of X-ray diffraction, differential scanning calorimetry, magnetization and electrical resistivity of the Zr_xZn_{1-x} alloys produced by sputter-deposition. We show the nonequilibrium phase diagram, the thermal stability, the magnetic and electron transport properties of vapor quenched Zr_xZn_{1-x} alloys.

II. Experimental Procedures

About $1 \mu m$ thick Zr_xZn_{1-x} alloy films with $x=0$ to 1 were produced on polyimide and acetylcellulose film substrates by a conventional rf sputtering method. Composite type targets were prepared from 99.99%Zr chips and 99.9%Zn disks. The substrate was maintained at about 350 K by indirect water cooling. The chemical compositions of sputter-deposited alloys were determined by an electron-probe microanalysis. The X-ray diffraction measurements were done at 300 K using Fe $K\alpha$ radiation and a carbon monochromator. The thermal stability was examined in an Ar atmosphere by means of differential scanning calorimetry (DSC) with a heating rate of 0.33 K/s. The magnetization was measured at 4.2 and 298 K by a torsion

* Graduate Student, Kyoto University, Kyoto 606, Japan.

** Department of Metal Science and Technology, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.

balance magnetometer. The electrical resistivity was measured by a four-probe DC method.

III. Results

Figure 1 shows the low angle parts of the X-ray diffraction patterns of vapor quenched $\text{Zr}_x\text{Zn}_{1-x}$ alloys. For $0.2 < x < 0.75$ a halo pattern is prominent, indicating an amorphous phase. On the other hand, for Zn-rich alloys with $0 \leq x < 0.1$, high angle peaks of the hcp structure are clearly observed, where the linewidths are much narrower than those of usual vapor quenched alloys. In Zn-rich hcp alloys the intensity ratios of diffraction peaks are similar to those of pure Zn powders, indicating no preferred orientation of grain growth usually observed in other sputter-deposited alloys. For Zr-rich alloys with $0.75 < x \leq 1$ the hcp peaks are observed. The observed broad linewidth is due to lattice defects and strains in vapor quenched alloys. A high index line was not observed except for $x=1$

Fig. 1 X-ray diffraction patterns of vapor quenched $\text{Zr}_x\text{Zn}_{1-x}$ alloys.

Fig. 2 Lattice constants, a and c , of vapor quenched hcp $\text{Zr}_x\text{Zn}_{1-x}$ alloys at room temperature.

probably because of a preferred orientation of grain growth.

Figure 2 shows the lattice constants, a and c , of vapor quenched hcp $\text{Zr}_x\text{Zn}_{1-x}$ alloys deduced from X-ray diffraction measurements. Both a and c values increase with increasing x . The c value obeys Vegard's law, while the a value does not.

Figure 3(a) and (b) show the surface morphology of vapor quenched $\text{Zr}_x\text{Zn}_{1-x}$ alloys. A rough surface of the Zn-rich alloy specimen is probably due to an effect of resputtering. On the other hand, the surface of the Zr-rich alloys has a smooth appearance. As shown in Fig. 3(c), the cross section of pure Zr metals shows a fibrous structure and an oblique deposition, which indicates the direction of the incident atom flux.

Figure 4(a) shows some examples of DSC traces of amorphous $\text{Zr}_x\text{Zn}_{1-x}$ alloys. A very broad hump of the exothermic heat in the intermediate temperature range may be ascribed to the structural relaxation, the desorption of incorporated Ar atoms and the release of residual strain in the sputter-deposited film. A sharp exothermic peak at high temperatures indicates the crystallization of the amorphous state, as confirmed by X-ray diffraction studies after these DSC measurements. Figure 4(b) shows the concentration dependence of the crystallization temperature, T_x , which is defined as the temperature corresponding to the

Fig. 3 Scanning electron micrographs of sputter-deposited Zr_xZn_{1-x} alloys: (a) Surface of the $Zr_{0.8}Zn_{0.2}$ alloy. (b) Surface of the pure Zr metal. (c) Cross section of the pure Zr metal.

onset of the exothermic peak in the DSC trace. The value of T_x is sensitive to Zr concentration and rapidly increases from 520 to 830 K with increasing x . For $x < 0.3$, further increase in temperature above T_x results in an endothermic heat at about 695 K. This occurs as a result of the melting of a precipitated Zn-rich primary solid solution.

Fig. 4 (a) Differential scanning calorimetry, DSC, traces obtained with a heating rate of 0.33 K/s for amorphous Zr_xZn_{1-x} alloys where the arrow indicates the crystallization temperature, T_x . (b) Crystallization temperature, T_x , obtained by DSC measurements of amorphous Zr_xZn_{1-x} alloys.

Fig. 5 Magnetization curves of the amorphous $Zr_{0.34}Zn_{0.66}$ alloy and the Laves phase $ZrZn_2$ ⁽⁷⁾.

Figure 5 shows the magnetization curve of the amorphous $Zr_{0.34}Zn_{0.66}$ alloy, in comparison with that of the Laves phase $ZrZn_2$ ⁽⁷⁾. Even at 4.2 K, the magnetization, M , of the amorphous alloy increases almost linearly with increasing applied magnetic field, H . The value of M is about 1×10^{-6} Wb m/kg (1×10^{-2} emu/

Fig. 6 Concentration dependence of the resistivity of vapor quenched Zr_xZn_{1-x} alloys at 4.2 K. $\circ$: amorphous phase; $\square$: single hcp phase; $\triangle$: Laves phase $ZrZn_2$ ⁽¹⁶⁾ produced by sintering.

g) at $H=8.0 \times 10^5$ A/m (10 kOe) and much smaller than that of the Laves phase, 4.3×10^{-4} Wbm/kg (3.4 emu/g)⁽⁷⁾.

Figure 6 shows the concentration dependence of the electrical resistivity at 4.2 K, $\rho_{4.2K}$, for vapor quenched Zr_xZn_{1-x} alloys, where large error bars are due to the difficulty in

Fig. 7 Temperature dependence of the electrical resistivity, $\rho/\rho_{4.2K}$, of Zr-rich hcp Zr_xZn_{1-x} alloys produced by vapor quenching.

measuring the film thickness with high accuracy. The value of $\rho_{4.2K}$ is always larger than about $2 \mu\Omega m$ except for $x \leq 0.1$ for both amorphous and crystalline alloys.

Figure 7 shows the temperature dependence of the electrical resistivity ratio, $\rho/\rho_{4.2K}$, for Zr-rich hcp Zr_xZn_{1-x} alloys. With increasing temperature, the reduced resistivity, $\rho/\rho_{4.2K}$, initially decreases and then shows a minimum at a low temperature. Above this minimum temperature, the temperature coefficient of resistivity, $TCR=(1/\rho)(d\rho/dT)$, is positive for all of the crystalline Zr-rich Zr_xZn_{1-x} alloys.

In contrast, TCR of the amorphous alloys shown in Fig. 8 is always negative between 4.2 and 270 K. The overall variation of $\rho/\rho_{4.2K}$ between 4.2 and 270 K increases with the increase in x , but it is about 8% of the absolute value of ρ even for $x=0.68$. Furthermore, it may be noted that the resistivity continues to increase even below 4.2 K, and apparently does not

Fig. 8 Temperature dependence of the electrical resistivity, $\rho/\rho_{4.2K}$, of amorphous Zr_xZn_{1-x} alloys produced by vapor quenching. The inset indicates the low temperature resistivity of the $Zr_{34}Zn_{66}$ alloy. The solid lines indicate the fitting curves to the empirical equation⁽²²⁾, $\rho=A+B \exp(-T/\Delta)$, obtained by a least square fitting between 30 and 270 K.

level off down to the lowest temperature of 1.3 K. This is illustrated in the inset in Fig. 8 for $x=0.34$.

IV. Discussion

1. Nonequilibrium phases and their structures

Figure 9 shows the nonequilibrium phase diagram of vapor quenched Zr_xZn_{1-x} alloys determined by X-ray diffraction measurements. For comparison, it also shows the result of the equilibrium Zr-Zn alloys at 300 K⁽⁵⁾. We have an amorphous phase for $0.2 < x < 0.7$ and hcp phases for $x < 0.1$ and $x > 0.75$.

Many lattice defects and strain are usually introduced in vapor quenched alloys prepared on water-cooled substrates. Zn-rich hcp alloys, however, show very sharp diffraction peaks, indicating a relatively small amount of lattice defects. The correlation between the morphology of thin films and the reduced substrate temperature, T_s/T_m , where T_s is the substrate temperature and T_m the melting point, has been discussed by Thornton⁽⁹⁾. For $T_s/T_m < 0.3$, a marked columnar structure with open boundaries has been observed, because the surface diffusion of adatoms is insufficient and a convex part of the growing film receives more incident flux (a shadowing effect). For $0.3 < T_s/T_m < 0.5$, where the surface diffusion dominates over the film growth, a dense columnar grain structure is observed. For $0.5 < T_s/T_m < 1$, where the bulk diffusion character-

izes the thin film structure, recrystallization and grain coarsening are observed. The results of X-ray diffraction measurements for the sputter-deposited Zr_xZn_{1-x} alloys are consistent with this classification of film growth mechanisms. In the Zn-rich region ($T_s/T_m \sim 0.5$), the vapor quenched alloys recrystallize and their grains grow. The substrate temperature of about 350 K is already high enough to enhance the atomic mobility of a low melting metal such as Zn. Furthermore, since the sputter-yield of Zn is one order of magnitude higher than that of Zr⁽¹⁰⁾, resputtering of Zn atoms from the deposited film may easily take place and possibly become responsible for the observed surface roughness in the Zn-rich alloys. In the Zr-rich region ($T_s/T_m \sim 0.15$), the grain growth along the direction of incident atom flux was observed on the SEM image (see Fig. 2 (c)) and many lattice defects are contained due to the insufficient atomic diffusion.

The amorphous phase has been obtained for $0.2 < x < 0.7$, where several intermetallic compounds exist in the equilibrium phase diagram⁽⁵⁾. The present results are consistent with those of other vapor quenched inter-transition metal amorphous alloys⁽²⁾⁻⁽⁴⁾, where intermetallic compounds are also found to exist in their equilibrium phase diagrams.

2. Crystallization temperature

The crystallization temperature, T_x , increases with the increase in Zr concentration. In vapor quenched Fe-Ti alloys, the value of T_x reaches its maximum at the composition corresponding to the Laves phase intermetallic compound⁽¹¹⁾. Here, the behavior observed in Zr_xZn_{1-x} alloys is quite different.

In the Zn-rich alloys the atomic diffusion may take place easily because of a substantial decrease in the melting temperature. Therefore, a sharp decrease in T_x with increasing Zn concentration shown in Fig. 4 suggests an important role of the atomic diffusion control process upon crystallization. In many alloys, the activation energy of the atomic diffusion is known to be proportional to the formation enthalpy of monovacancy, ΔH_v , of the atom with a smaller size⁽¹²⁾⁽¹³⁾. An empirical relation be-

Fig. 9 (a) Nonequilibrium phase diagram of vapor quenched Zr_xZn_{1-x} alloys where the hatched region indicates the two phase region. (b) equilibrium phase diagram of Zr-Zn alloys at room temperature⁽⁵⁾.

Fig. 10 Crystallization temperature, T_x , as a function of formation enthalpy of monovacancy, ΔH_h , of the smaller size atom, $Zn^{(11)(12)}$. The solid line indicates $T_x = 8.4 \cdot \Delta H_h$.

tween T_x and ΔH_h has been found for many amorphous alloys⁽¹³⁾⁽¹⁴⁾: $T_x = k \cdot \Delta H_h$, where k is an empirical constant of about 7 for T_x in K and ΔH_h in kJ/mol. Figure 10 shows T_x as a function of ΔH_h in the present amorphous Zr_xZn_{1-x} alloys. The data fall on a straight line with a slope of 8.4, being in good agreement with the above relation.

3. Magnetism of the amorphous phase

As shown in Fig. 5, the amorphous $Zr_{34}Zn_{66}$ alloy, whose concentration corresponds to the Laves phase $ZrZn_2$, is apparently paramagnetic. The low temperature heat capacity has been measured⁽⁸⁾⁽¹⁵⁾ for the Laves phase $ZrZn_2$ and amorphous $ZrZn_2$ alloys. The electronic specific heat coefficient, γ , is large in the Laves phase $ZrZn_2$, indicating the high electron density of states at the Fermi level, $N(E_F)$. This is believed to be responsible for the occurrence of a weak itinerant electron ferromagnetism. In the amorphous alloys, on the other hand, the γ value is much smaller than that of the Laves phase. Therefore, $N(E_F)$ in the chemically disordered state may be too low for the onset of ferromagnetism in the amorphous Zr_xZn_{1-x} alloys.

4. Electrical resistivity

The large residual resistivity in the bulk Laves phase $ZrZn_2$ alloy produced by sintering⁽¹⁶⁾ is partially due to the sample preparation method. In vapor quenched Zr_xZn_{1-x} alloys

the resistivities of both amorphous and Zr-rich hcp crystalline phases are larger than that of the Laves phase $ZrZn_2$ probably because of a high degree of atomic disorder and a large amount of lattice defects.

A negative TCR has been observed in many amorphous alloys. Mooij has found that the sign and value of TCR empirically correlate with the magnitude of resistivity at room temperature in the transition metal alloys: TCR is positive for $\rho < 1.5 \mu\Omega m$, while TCR negative for $\rho > 1.5 \mu\Omega m$ ⁽¹⁷⁾. As shown in Fig. 6, the present amorphous Zr_xZn_{1-x} alloys show large ρ values and negative TCR at room temperature, being satisfied with Mooij's correlation. However this empirical relation cannot be applied to Zr-rich hcp Zr_xZn_{1-x} alloys, which show positive TCR at room temperature in spite of their large ρ values.

According to the Faber-Ziman theory⁽¹⁸⁾⁽¹⁹⁾, liquid and amorphous alloys have a negative TCR when the ratio $2k_f/k_p \sim 1$, where k_f is the Fermi wave number and k_p the wave number corresponding to the first peak of the structure factor. Meisel and Cote⁽²⁰⁾ have predicted that a reduction of the electron mean free path extends the range of $2k_f/k_p$ favorable for a negative TCR. In the high resistivity limit, the $(1-AT^2)$ -dependence of the resistivity is predicted to occur at low temperatures because of the reduction of the inelastic electron-phonon interaction. The electron transport properties of simple amorphous alloys are well explained by the generalized Faber-Ziman theory. In the present amorphous Zr_xZn_{1-x} alloys, however, the $(1-AT^2)$ -dependence of electrical resistivity was not observed at low temperatures. Similar low temperature behavior has also been observed in the amorphous alloys containing appreciable d-electrons at the Fermi level. In these amorphous alloys the following empirical equation has been proposed for the temperature dependence of the electrical resistivity: $\rho = A + B \exp(-T/\Delta)$ ⁽²¹⁾. As shown in Fig. 8, the temperature dependence of amorphous Zr_xZn_{1-x} alloys with $x \geq 0.3$ well obeys this relation, suggesting the substantial contribution of d-electrons to electron transport phenomena.

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