Viscous Flow Workability of Ni-Cr-P-B Metallic Glasses Produced by Melt-Spinning in Air

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We prepared the $\text{Ni}_{80-x}\text{Cr}_x\text{P}_{16}\text{B}_4$ ($x = 3, 6, 9, 12, 15, 18, 21, 24, 27$ and $30 \text{ at\%}$) alloy ingots in an Ar flow atmosphere and then produced the alloy ribbons by melt-spinning. The thermal stability was examined and the alloy composition was optimized.

A supercooled liquid state was observed in the alloys with Cr contents above 9 at% and the T_g and T_x increased with increasing Cr content. There is a tendency for ΔT_x to increase with increasing Cr content up to 18 at%. The largest ΔT_x is about 45 K and remains almost unchanged in the Cr content range above 15 at%. The groove-forming tests were performed for the alloy with optimized compositions. The $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ glassy alloy was heated up to T_g and was deformed by hot-pressing with dies in the supercooled liquid state. The alloy possessed a single glassy phase and the thermal stability parameters, T_g , T_x and ΔT_x of the alloy did not change even after the hot-pressing. Thus, the Ni-based glassy alloy was not thermally affected by the hot-pressing treatment in the present experimental condition. Finally, we successfully produced the metallic glassy separator for Proton Exchange Membrane Fuel Cell (PEMFC) by hot-pressing in the supercooled liquid state.

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1. Introduction

In 1968, Chen and Turnbull found experimentally that the specific heat of the rapidly solidified Au-Ge-Si amorphous alloy changed discontinuously at a certain temperature, which corresponds to the glass transition behavior.¹⁾ After this discovery, the amorphous alloys having the distinct glass transition have been named as the metallic glasses. Inoue *et al.* have found a large number of glassy alloys consisting of metallic components with a large supercooled liquid region in various multi-component metallic alloys since 1988.²⁻⁵⁾ These bulk glassy alloys have been obtained at relatively low cooling rates of less than $100 \text{ K}\cdot\text{s}^{-1}$ from liquid state by use of stabilization of the supercooled liquid state against crystallization. The stabilization has enabled the production of bulk glassy alloys in the thickness range of 1–100 mm by using various casting processes.

In general, the thermal stability of amorphous alloys is too low to be worked into various shapes at elevated temperatures. Besides, amorphous alloys cannot keep good ductility when they are heated to the crystallization temperature T_x . Consequently, the applications of amorphous alloys have been limited to small size products such as tapes, wires and powders. On the contrary, metallic glasses exhibit the supercooled liquid state in the temperature range lower than T_x . The existence of the supercooled liquid state leads to great advantage for industrial applications.⁶⁾ That is, glassy alloys are promising materials for structural applications because of high mechanical strength, high fracture toughness and good corrosion resistance.

It is preferable to prepare the mother alloy ingots and to produce the melt-spun samples in a controlled atmosphere with pure inert gases such as Ar. In general, sample surfaces are oxidized, or crystallization behavior is changed by dissolving oxygen into the alloy if the sample is produced in an atmosphere without evacuation or in air. However,

Some amorphous alloys have been produced in air. For example, the Fe-Si-B amorphous alloys, having excellent soft-magnetic properties, can be produced and are commercially available since 1975. If a glassy alloy is processed in air ((1) production of a mother alloy ingot, (2) melt-spinning of glassy samples and (3) viscous flow deformation of glassy samples in a supercooled liquid state), we can decrease the process cost for glassy alloy applications, leading to the expectation of mass-production of glassy alloys.

A large number of Ni-based amorphous alloys such as Ni-B,⁷⁾ Ni-P,⁸⁾ Ni-Zr⁹⁾ binary alloys and Ni-P-B,¹⁰⁾ Ni-Si-B,¹¹⁾ Ni-Al-B,¹²⁾ Ni-M-B ($M = \text{Cr}$ or Mo)¹³⁾ and Ni-M-C ($M = \text{Cr}, \text{Mo}$ or W)¹⁴⁾ ternary ones have been developed up to date. It is well known that the Ni-based metallic glasses possess extremely high mechanical strength. For example, it was reported that the rod-shaped glassy samples of 3 mm in diameter in the Ni-Nb-Ti-Zr-Co-Cu system could be formed by Cu mold casting and the maximum mechanical strength was about 3 GPa.¹⁵⁾ Furthermore, Hashimoto *et al.* reported that the Ni-Cr-P-B quaternary glassy alloys possessed excellent corrosion resistance.¹⁶⁾ Recently we found that this quaternary alloy could be melt-spun in air without any degradation of thermal and other properties. It is important to optimize an alloy composition of the Ni-Cr-P-B glassy alloy having a large supercooled liquid region and to examine the viscous flow workability of the optimized alloy in various atmospheres.

In this work, we prepared the mother alloy ingots by using a high-frequency induction coil furnace in an Ar flow atmosphere without evacuation and subsequently produce the melt-spun samples in a dilute Ar atmosphere or in air. Then we examined the glass transition behavior of the alloys and optimized the glassy alloy compositions. After that, the groove-forming behavior is examined by hot-pressing at around the glass transition temperature T_g , with the aim of investigating the possibility of producing a metallic glassy separator for proton exchange membrane fuel cells (PEMFC) by this method.¹⁷⁾

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2. Experimental

The ingots of the $\text{Ni}_{80-x}\text{Cr}_x\text{P}_{16}\text{B}_4$ ($x = 3, 6, 9, 12, 15, 18, 21, 24, 27$ and $30\text{at\%}$) alloys were prepared in an Ar flow atmosphere by a high-frequency induction coil furnace without evacuation by using a pump. Tape-shaped samples of these alloys were produced by a single-roller melt-spinning technique in a dilute Ar atmosphere or in air. The melt-spun ribbon samples of about 1–10 mm in width and 10–50 μm in thickness were produced in air. The 50 mm wide melt-spun ribbon sample was produced in a dilute Ar atmosphere.

The amorphicity of the melt-spun samples was examined by X-ray diffractometry (hereafter denoted as XRD) with $\text{Cu-K}\alpha$ radiation (RIGAKU RAD-B, 40 kV, 30 mA). Thermal stability of the melt-spun samples was examined by differential scanning calorimetry (hereafter denoted as DSC) at a heating rate of 0.67 K/s in an Ar flow atmosphere (DSC6300, Seiko Instruments Inc.). T_g and T_x were estimated by the measurement software (Muse standard analysis, SII (Seiko Instruments Inc.) Nano Technology Inc.). The Vickers hardness was measured with a load of 25 g. Prior to corrosion tests, the specimens were mechanically polished with SiC paper. The specimens were 140 mm in length, 10 mm in width and 30 μm in thickness. The specimens were immersed in the dilute sulfuric acid solution of 1 mass% H_2SO_4 at 353 K without stirring. Both sides of the surface of the specimen were exposed to the solution. The corrosion rates were calculated from the weight reduction of the specimen after a certain immersion time.

The groove-forming tests were performed by a hot-pressing with precisely groove-formed dies in a dilute Ar atmosphere or in air at around T_g . Three types of dies were used in this work. Figures 1(a) and (b) show schematic illustrations of the grooves carved on the dies. One can see wave-like semicircular grooves having a pitch of 8 mm and a depth of 4 mm in Fig. 1(a) and comb-like precise grooves having a pitch of 1.52 mm and a depth of 0.76 mm in Fig. 1(b). Moreover, Fig. 1(c) shows a groove pattern that we used to produce PEFC separators by hot-pressing with the dies. The separator flow pattern was designed by Electrochem, Inc. (U.S.). The gap between the upper and lower dies used in this work is 50 μm .

3. Results and Discussion

We examined optimum compositions having the largest supercooled liquid region in the $\text{Ni}_{80-x}\text{Cr}_x\text{P}_{16}\text{B}_4$ ($x = 3, 6, 9, 12, 15, 18, 21, 24, 27$ and $30\text{at\%}$) alloys. Figures 2(a) and (b) show the examples of the XRD patterns and the DSC curves of the Ni-Cr-P-B alloy samples, respectively. All the melt-spun samples have a single amorphous/glassy phase, as is evident from a broad halo peak that is inherent to amorphous phase. It is also seen in Fig. 2(b) that a supercooled liquid region is observed in the alloys with Cr contents of more than 9 at% and the T_g and T_x increase with increasing Cr content.

Figure 3 shows the summarized plot of thermal stability parameters, T_g , T_x and the supercooled liquid region ΔT_x ($= T_x - T_g$) of the samples as a function of Cr content for the samples. There is a tendency for ΔT_x to increase with

Fig. 1 Schematic illustrations of the dies used for hot-pressing in this work. (a) Wave-like rough grooves, (b) comb-like precise grooves and (c) the serpentine-type flow pattern grooves for PEFC separators. (Caution: Commercial use of this separator flow pattern design is prohibited without permission of Electrochem, Inc. (U.S.).)

increasing Cr content up to 18 at%. The saturated value of ΔT_x is about 45 K at around 15–18 at% and remains unchanged with further increasing Cr content. The aim of this work is to examine the groove-forming ability for the compositionally optimized alloy. In the viewpoint of mass-production, it is preferable to use the alloy with the ΔT_x as

Fig. 2 XRD patterns (a) and DSC curves (b) of melt-spun $\text{Ni}_{80-x}\text{Cr}_x\text{P}_{16}\text{B}_4$ ($x = 3, 6, 9, 12, 15, 18, 21, 24, 27$ and 30) alloy samples.

large as possible and also the T_g as low as possible. In this point of view, the $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ glassy alloy was chosen as an optimized one. Therefore, the groove-forming tests were performed with the melt-spun $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ glassy alloy produced in air.

Table 1 summarizes the corrosion resistance data for the $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ and $\text{Ni}_{56}\text{Cr}_{24}\text{P}_{16}\text{B}_4$ glassy alloys in compar-

Fig. 3 Summarized plot of the T_g , T_x and ΔT_x of the melt-spun alloy samples as a function of Cr content. The direction of the arrows indicates the vertical axis that the curve should refer to.

Table 1 Corrosion resistance of melt-spun $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ and $\text{Ni}_{56}\text{Cr}_{24}\text{P}_{16}\text{B}_4$ glassy alloys. The data of the high corrosion-resistant stainless steel, SUS316L are also shown for comparison.

Alloy composition (at.%)	Corrosion rate (mm/year)
$\text{Ni}_{56}\text{Cr}_{24}\text{P}_{16}\text{B}_4$	9.52×10^{-4}
$\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$	6.94×10^{-3}
SUS316L	1.48×10^{-2}

ison with the high corrosion resistant stainless steel, SUS316L (purchased from the NILACO corporation, Japan). The corrosion rates of the $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ and $\text{Ni}_{56}\text{Cr}_{24}\text{P}_{16}\text{B}_4$ glassy alloys are 6.94×10^{-3} and 9.52×10^{-4} mm/y, respectively. There is a tendency that the corrosion rate decreases with increasing Cr content. These values are much smaller than that of SUS316L, indicating that the Ni-Cr-P-B glassy alloys possess excellent corrosion resistance.

The $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ and $\text{Ni}_{56}\text{Cr}_{24}\text{P}_{16}\text{B}_4$ glassy alloys possess the Vickers hardness (Hv) of 829 and 844, respectively. Those values are much higher than that for the SUS316L (Hv = 399). It was also confirmed that these glassy alloys could be bent through 180 degrees without fracture at room temperature.

Figure 4 shows a cross-section of the sample hot-pressed with the dies having wave-like grooves shown in Fig. 1(a) at 659 K ($= T_g$). Nearly complete plastic deformation is achieved as clearly shown in this figure.

Amorphicity and thermal stability of the sample before and after the hot-pressing were examined. Figure 5(a) shows the XRD patterns of the samples before and after the hot-pressing. The sample possesses a single glassy phase even after the hot-pressing. The DSC curves of the samples before and after the hot-pressing are also shown in Fig. 5(b). The supercooled liquid region is observed in the DSC curve for the hot-pressed sample. The thermal stability parameters, T_g , T_x and ΔT_x of the alloy remain almost unchanged even after the hot-pressing, indicating that the sample is not thermally affected by hot-pressing in this experimental condition.

Fig. 4 A cross-sectional view of the $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ glassy alloy sample hot-pressed with the wave-like groove dies.

Fig. 5 XRD patterns (a) and DSC curves (b) of the melt-spun $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ glassy alloy samples before and after the hot-pressing.

Figure 6 shows an outer and a cross-sectional views of the sample hot-pressed by using the dies with precise comb-like grooves shown in Fig. 1(b) at 659 K ($= T_g$). It is confirmed

Fig. 6 Optical micrographs of the $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ glassy alloy sample hot-pressed with the comb-like precise groove dies. (a) Outer shape and (b) Cross-section.

Fig. 7 Optical micrograph of the $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ glassy alloy separator for the PEMFC produced by hot-pressing in air.

that the precise grooves are successfully formed by viscous flow in the supercooled liquid region. Thus, the $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ glassy alloy has an excellent groove-formability. The depth of the grooves formed on the hot-pressed sample is 0.6 mm.

Finally we tried to make a separator for the PEMFC having the precise grooves (pitch: 1.52 mm and depth: 0.76 mm) in air. The 50 mm wide melt-spun glassy sample was used for this hot-pressing test. Figure 7 shows an outside view of the glassy separator groove-formed by the hot-pressing with the dies having the serpentine flow patterns shown in Fig. 1(c). It was found that precise grooves for separator were formed and that this alloy was processable in air without significant surface oxidation. From these results, it was found that the $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ glassy alloy can be produced by melt-spinning

in air and also can be deformed in air in the supercooled liquid state at around T_g , resulting in good suitability for mass-production. These results indicate the possibility for future practical use of the Ni-based glassy alloys for precisely designed application such as a separator of PEMFC.

4. Conclusions

We prepared the $\text{Ni}_{80-x}\text{Cr}_x\text{P}_{16}\text{B}_4$ ($x = 3, 6, 9, 12, 15, 18, 21, 24, 27$ and $30 \text{ at\%}$) alloy ingots in an Ar flow atmosphere and then produced the alloy ribbons by melt-spinning. The workability of the alloy in the supercooled liquid state was examined. The conclusions obtained in this work are as follows.

(1) All the melt-spun alloys had a single amorphous/glassy phase. A supercooled liquid state was observed in the alloys with Cr content of more than 9 at% and the T_g and T_x increased with increasing Cr content. There is a tendency for ΔT_x to increase with increasing Cr content up to 18 at%. The saturated value of ΔT_x was about 45 K.

(2) The corrosion rates of the $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ and $\text{Ni}_{56}\text{Cr}_{24}\text{P}_{16}\text{B}_4$ glassy alloys are 6.94×10^{-3} and $9.52 \times 10^{-4} \text{ mm/y}$, respectively. Those values are smaller than that of SUS316L. The $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ and $\text{Ni}_{56}\text{Cr}_{24}\text{P}_{16}\text{B}_4$ glassy alloys possess the Vickers hardness (Hv) of 829 and 844, respectively. These glassy alloys can be bent through 180 degrees without fracture at room temperature.

(3) The $\text{Ni}_{65}\text{Cr}_{15}\text{P}_{16}\text{B}_4$ glassy alloy had an excellent groove-formability. The precise grooves were successfully formed by hot-pressing in the supercooled liquid state. A single glassy phase was maintained and the thermal stability parameters, T_g , T_x and ΔT_x of the alloy did not change even after the hot-pressing at around T_g . Thus, the sample is not

thermally affected by hot-pressing in the present experimental condition. Finally, we successfully produced the metallic glassy separator for PEMFC by hot-pressing in the supercooled liquid state in air. It was found that this alloy could be processed in air.

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