Formation, Thermal Stability and Mechanical Properties of Aluminum-Based Glassy Alloys Containing Boron

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Glassy type Al-based alloys, with a distinct glass transition and a supercooled liquid region before crystallization, were formed in (Al0.84Ni0.16)Ce0.0684Ce0.1005B, (x = 0 to 10 at%) and (Al0.84Ni0.16Y0.09Ce0.02)1-xB, (x = 0 to 3 at%) systems by melt spinning. The addition of an optimum amount of B was found to increase the temperature interval of supercooled liquid region from 18 K to 23 K at 6%B for the former system and from 28 K to 31 K at 1.5 and 2% B for the latter system. The similar increase with B content was also recognized for Vickers hardness \( H_v \) and tensile fracture strength \( \sigma_t \) and the highest values of \( H_v \) and \( \sigma_t \) are 400 and 1060 MPa, respectively, at 6% B and 375 and 1140 MPa, respectively, at 1.5% B. The maximum phenomena of temperature interval of supercooled liquid region \( \Delta T_s = T_s - T_m \), \( H_v \) and \( \sigma_t \) at optimum B contents can be interpreted in the framework of the three empirical component rules for the stabilization of supercooled liquid and the formation of bulk glassy alloys. The crystallization occurs through two stages of glass \( \rightarrow \) Al + metastable phase \( \rightarrow \) Al + AlNi + AlCe for the Al-Ni-Ce-6%B alloy and through three stages of glass \( \rightarrow \) Al + glass \( \rightarrow \) Al + metastable phase + glass \( \rightarrow \) Al + Al4C3 + Al3Y + Al6NiY + Al-Y-Ni-Co quaternary compound for the Al-Ni-Y-Co-2%B alloy. The finding of Al-based glassy alloys with large \( \Delta T_s \) values above 30 K is encouraging for future development of Al-based alloys as a high strength material with light weight.

Keywords: aluminum-based alloy, glassy phase, boron addition, glass transition, supercooled liquid region, mechanical strength

1. Introduction

It is well known that Al-based amorphous and glassy alloys with high strength and good ductility can be synthesized in Al-RE (RE = rare earth metal) binary \(^1\)-\(^3\) and Al-RE-LTM (LTM = VI-VIII group late transition metal) \(^4\)-\(^7\) and Al-ETM-LTM (ETM = IV-V group early transition metal) \(^8\),\(^9\) ternary systems by liquid quenching. Although the maximum sample thickness for glass formation has been reported to be about 500 \( \mu \)m for Al-Ni-Y-Co system,\(^10\) the tensile fracture strength reaches as high as 1000 to 1250 MPa for the Al-RE-LTM type glassy alloys in conjunction with good ductility as is shown by the complete bending through 180 degrees without fracture.\(^10\)-\(^12\) The glass-forming ability has been interpreted to result from the combination of two factors, i.e., significant atomic size mismatches above 12% and large negative heats of mixing, as is evidenced from the large atomic size ratios of 0.68 to 0.87 for Al-RE(Y,Ce), RE-LTM(Ni,Co) and Al-LTM atomic pairs and large negative heats of mixing ranging from -18 to -38 kJ/mol for their atomic pairs.\(^13\),\(^14\) The strong negative heats of mixing result in the achievement of such high tensile fracture strength, but the strong bonding nature is unfavorable for the formation of Al-based glassy alloys with good ductility in a wide Al concentration range. There have been no data on the influence of an additional element with positive heat of mixing against Al on the formation and fundamental properties of Al-based glassy alloys, though its addition is expected to extend an amorphous composition range and to decrease mechanical strength. The metalloid element of B has a positive heat of mixing of 15 kJ/mol against Al\(^15\) and a significant difference in atomic size ratio to Al.\(^13\) The addition of a rather large amount of B also has an advantage leading to a decrease in specific weight of the resulting alloys. This paper intends to present the formation, thermal stability and mechanical properties of Al-Ni-Ce-B quaternary and Al-Ni-Y-Co-B pentad glassy alloys and to investigate the effect of addition B element on their properties.

2. Experimental Procedure

Multi-component Al-based alloy ingots in Al-Ni-Ce-B and Al-Ni-Y-Co-B systems were produced by arc melting the mixtures of pure Al (99.99 mass%), Ni (99.9%), Co (99.9%), Ce (99.9%) and Y (99.9%) metals and B (99.5%) crystal in an argon atmosphere. The alloy compositions represent nominal atomic percentages. From the alloy ingots, glassy alloys in a ribbon form with a cross section of 0.02 x 1.0 mm\(^2\) were produced by the melt spinning technique. The structures in as-spun and annealed states were examined by X-ray diffraction using monochromatic CuK\(_{\alpha}\) radiation and transmission electron microscopy (TEM) linked with energy dispersive spectroscopy (EDS). Thermal stability associated with glass transition, supercooled liquid region and crystallization was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Tensile fracture strength of the melt-spun ribbon samples was measured at room temperature with an Instron test machine. The gauge dimension of the test specimen was 10 mm in length and the strain rate was 8.3 x 10\(^{-4}\) s\(^{-1}\). Vickers hardness was also measured with a Vickers microhardness indenter under a load of 0.245 N. Fracture surface was examined by scanning electron microscopy (SEM).

3. Results

Figure 1 shows the B concentration ranges in which glassy and amorphous phases are formed in the melt-spun Al-Ni-Ce-B, Al-Ni-Y-B and Al-Ni-Y-Co-B alloys. The features of this figure are summarized as follows; (1) The glassy alloys were obtained in the wide B concentration range when the
The constituent ratios of the metallic elements were fixed to \((\text{Al}_{84}\text{Ni}_{10}\text{Ce}_{6})\) and \((\text{Al}_{84}\text{Ni}_{5}\text{Y}_{9}\text{Co}_{2})\), (2) The replacement of Ce or Y by B is much harmful for the formation of a glassy phase as compared with the replacement of Ni by B, and (3) Al-based glassy alloys are formed in a wide B concentration range up to at least 10 at% B. Figure 2 shows the DSC curves of the melt spun \((\text{Al}_{0.84}\text{Ni}_{0.05}\text{Y}_{0.09}\text{Co}_{0.02})_{100-}\text{x}\text{B}_{\text{x}}\) glassy alloys. All the alloys exhibit the glass transition, followed by a small supercooled liquid region, a large exothermic peak and then two small exothermic peaks. As the B content increases to 10 at%, the glass transition temperature \((T_g)\) and crystallization temperature \((T_x)\) decrease gradually and the second exothermic peak tends to be broadened. It is seen that the decrease in \(T_g\) is larger than that of \(T_x\) in the B concentration range below 6 at%, leading to a slight increase in the supercooled liquid region defined by the difference between \(T_g\) and \(T_x\), \(\Delta T_x = T_x - T_g\). The change in \(T_g\), \(T_x\) and \(\Delta T_x\) with B content is shown in Fig. 3, together with the data of Vickers hardness \((H_v)\) and tensile fracture strength \((\sigma_f)\). All the properties of \(\Delta T_x\), \(H_v\) and \(\sigma_f\) increase in the B concentration range up to 6 at% and the highest values of \(\Delta T_x\), \(H_v\) and \(\sigma_f\) are 23 K, 400 and 1060 MPa, respectively.

We further examined the precipitation phases corresponding to the three exothermic peaks on the DSC curves shown in Fig. 2. Figure 4 shows X-ray diffraction patterns of the \((\text{Al}_{0.84}\text{Ni}_{0.10}\text{Ce}_{0.06})_{100-}\text{x}\text{B}_{\text{x}}\) glassy alloys heated for 600 s at 567 K, 613 K and 627 K corresponding to the first, second and third exothermic peaks, respectively. The diffraction peaks can be identified as fcc-Al and unknown phases for the sample heated at 567 K and Al, \(\text{Al}_3\text{Ni}\) and \(\text{Al}_4\text{Ce}\) phases for the samples heated at 613 and 627 K. The precipitates due to the first exothermic peak consist mainly of a metastable unknown phase. The second exothermic peak corresponds to the decomposition of the metastable phase to Al, \(\text{Al}_3\text{Ni}\) and \(\text{Al}_4\text{Ce}\) phases and the third exothermic peak appears to result from grain growth reaction of the three constituent phases. We could not observe any precipitates of borides even for the Al-based alloys containing 6 at% B.

Figure 5 shows the DSC curves of the \((\text{Al}_{0.84}\text{Ni}_{0.05}\text{Y}_{0.09}\text{Co}_{0.03})_{100-}\text{x}\text{B}_{\text{x}}\) glassy alloys. These glassy alloys exhibit the sequential transition of glass transition, supercooled liquid region and then crystallization reactions consisting of three exothermic peaks. The phase transition of the glassy phase to an equilibrium structure appears to occur through three
stages. As the B content increases from 0% to 2 at%, the $T_g$ and $T_x$ decrease from 554 to 542 K and 582 to 573 K, respectively, while $\Delta T_x$ increases from 28 to 31 K. It is important to point out that the $\Delta T_x$ value exceeding 30 K for the 2%B-containing alloy is the largest among all Al-based glassy alloys. Figure 6 shows the $T_g$, $T_x$, $\Delta T_x$, $H_v$ and $f$ as a function of B content for the (Al$_{0.84}$Ni$_{0.10}$Ce$_{0.06}$)$_{100-x}$B$_x$ glassy alloys. The $\Delta T_x$ shows a maximum value of 31 K at 1.5 and 2 at%. It is seen that the $H_v$ and $f$ also show maximum values of 375 and 1140 MPa, respectively, at 1.5 and 2 at% B and decrease significantly with further increasing B content. One can notice the same B concentration dependence among $\Delta T_x$, $H_v$ and $f$, in agreement with the tendency for the (Al$_{0.84}$Ni$_{0.10}$Ce$_{0.06}$)$_{100-x}$B$_x$ glassy alloys shown in Fig. 3.

Figure 7 shows X-ray diffraction patterns of the 2%B-containing alloy samples heated for 600 s to 577 K, 616 K and 688 K corresponding to the temperatures just above the first, second and third exothermic peaks, respectively. The diffraction peaks can be identified as fcc-Al + glassy phases for the sample heated at 577 K, Al + metastable phase + glassy phases for the sample heated at 616 K and Al + Al$_2$Co$_2$ + Al$_3$Y + AlNiY phases for the sample heated at 688 K. As shown in Fig. 8(a), the plate-like phase with a width of 50 nm and a length of 300 nm precipitates in coexistent with Al, Al$_2$Co$_2$, Al$_3$Y and Al$_3$Ni$_3$Y phases. TEM observation and EDS analysis shown in Fig. 8 indicate that the composition of the plate-like phase is Al$_{75}$Y$_{10}$Ni$_{10}$Co$_{5}$. This plate-like quaternary phase was previously observed by Bassim et al. and Kawamura et al. A d spacing of this phase is about 2.5 nm from selected-area diffraction pattern (SADP) shown in inset of Fig. 8(a) and this d spacing is nearly consistent with previous data (~2.7 nm). Thus, the structure of the plate-like quaternary compound is considered to be similar to the Al$_{16}$Ni$_{13}$Y crystal structure. It is thus concluded that the first large exothermic peak is due to the precipitation of Al phase from the glassy matrix and the second small peak results from the precipitation of metastable phase from the remaining glassy phase. The glassy phase is remaining even after the second exothermic reaction stage and the significant third exothermic peak is due to the decomposition of the metastable phase as well as the disappearance of the remaining glassy phase, accompanying
the precipitation of Al, Al\textsubscript{9}Co\textsubscript{2}, Al\textsubscript{3}Y, Al\textsubscript{4}NiY and Al-Y-Ni-Co quaternary phases. Although the glass transition, followed by the supercooled liquid region is observed for the Al-Ni-Ce-B and Al-Ni-Y-Co-B glassy alloys, the crystallization mode is significantly different between both the alloys. It is thus noticed that the largest $\Delta T_x$ value for Al-based glassy alloys is obtained for the Al-Ni-Y-Co-2%B alloy with the multi-stage crystallization mode.

4. Discussion

It was shown in section 3 that the $\Delta T_x$ values of the Al-Ni-Ce and Al-Ni-Y-Co glassy alloys increased from 18 K at 0%B to 23 K at 6%B and from 28 K at 0%B to 31 K at 2%B, respectively, and then decreased significantly with further increasing B content. The $\Delta T_x$ value of 31 K is believed to be the largest for all Al-based glassy alloys reported up to date. It is therefore important to discuss the reason for the increase in $\Delta T_x$ by the addition of the optimum B content (about 2 at%). As described above, the formation of a glassy phase in Al-Ni-Ce and Al-Ni-Y-Co systems has been interpreted\textsuperscript{10,17} to result from the satisfaction of the three component rules,\textsuperscript{18–21} i.e., (1) multi-component consisting of more than three elements, (2) significant atomic size mismatches above 12% among the main three elements, and (3) negative heats of mixing among their elements. The atomic size ratios of Al, Ce, Y, Ni and Co to B are 1.59, 2.03, 2.02, 1.39 and 1.39,\textsuperscript{13} respectively. The B element has significant atomic size mismatch ratios above 12% against all the other constituent elements and satisfies the atomic size rule. However, the heat of mixing for B is negative to Ni (−9 kJ/mol), Co (−9 kJ/mol), Ce (−33 kJ/mol) and Y (−35 kJ/mol) elements while the Al-B atomic pair has a positive heat of mixing (+15 kJ/mol),\textsuperscript{14} leading to the deviation from the three empirical rules. It is therefore interpreted that the increase in $\Delta T_x$ in the low B concentration ranges is due to the satisfaction of the atomic size rule and the decrease in $\Delta T_x$ in the higher B concentration range originates from the increase in the contribution of Al-B atomic pair with positive heat of mixing.

In addition to $\Delta T_x$, it is noticed that the $H_v$ and $\sigma_t$ also increase in the low B concentration ranges. The increases in $H_v$ and $\sigma_t$ are presumably due to the formations of Ni-B, Co-B, Ce-B and Y-B pairs with negative heats of mixing as well as the more optimization of the atomic size mismatch rule.
The similar tendency has been also observed for Cu-Zr-Ti base alloys in which the addition of Be of about 10 at% in Cu-Zr-Ti base glassy alloy caused an increase in the glass-forming ability and the tensile fracture strength. In that case, the heat of mixing is 0 kJ/mol for Cu-Be pair and negative for Zr-Be and Ti-Be pairs. The addition of more than 10 at% Be caused the rapid decrease in glass-forming ability.

5. Summary

We examined the effect of B addition on the formation tendency, thermal stability and mechanical properties of melt-spun \((\text{Al}_{0.84}\text{Ni}_{0.05}\text{Y}_{0.09}\text{Co}_{0.02})_{100-x}\text{B}_x\) and \((\text{Al}_{0.84}\text{Ni}_{0.05}\text{Y}_{0.09-}\text{Co}_{0.02})_{100-x}\text{B}_x\) glassy alloys. The results obtained are summarized as follows:

1. A glassy phase with glass transition was obtained in the B concentration ranges up to 10 at% for the Ce-containing alloys and 3 at% for the Y-containing alloys.
2. The \(T_g\) and \(T_x\) decrease slightly with increasing B content and the decrease of \(T_g\) is larger than that of \(T_x\), leading to an increase in \(\Delta T_s\). The largest \(\Delta T_s\) was 23 K at 6%B for the former alloy system and 31 K at 2%B for the latter system. The \(\Delta T_x\) value of the \((\text{Al}_{0.84}\text{Ni}_{0.05}\text{Y}_{0.09-}\text{Co}_{0.02})_{100-x}\text{B}_x\) alloy was the largest for all Al-based glassy alloys reported up to date.
3. The \(H_v\) and \(\sigma_t\) also increase with increasing B content in the low B content ranges up to 6%B for the Ce-containing alloys and 2 at%B for the Y-containing alloys. The highest values of \(H_v\) and \(\sigma_t\) are 400 and 1060 MPa, respectively, at 6%B for the former alloy and 375 and 1140 MPa, respectively, at 1.5 and 2%B for the latter alloy.
4. The primary crystallization reaction is due to the formation of mixed fcc-Al and metastable unknown phases for the Al-Ni-Ce-6%B alloy and Al and remaining glassy

![Fig. 7 X-ray diffraction patterns of the \((\text{Al}_{0.84}\text{Ni}_{0.05}\text{Y}_{0.09}\text{Co}_{0.02})_{98}\text{B}_2\) glassy alloy heated for 600 s at 577, 616 and 688 K corresponding to the temperatures just above the first, second and third exothermic peaks, respectively.](image)

![Fig. 8 (a) Bright-field transmission electron micrograph and SADP (inset) of the \((\text{Al}_{0.84}\text{Ni}_{0.05}\text{Y}_{0.09}\text{Co}_{0.02})_{98}\text{B}_2\) alloy in annealed state for 600 s at 688 K (third crystallization peak). (b) Energy dispersive spectroscopy (EDS) spectra taken from the plate-like phase indicated by the arrow in the TEM image.](image)
phases for the Al-Ni-Y-Co-2%B alloy. Their primary crystalline phases remain unchanged over the whole B content ranges examined in the present study.

(5) The syntheses of Al-based glassy alloys with high fracture strength exceeding 1000 MPa and large supercooled liquid region above 30 K are promising for future development of high-strength Al-based bulk alloys with glassy or nanocrystalline phase.

REFERENCES