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Production of Al-based Amorphous Alloys by a Metallic Mold Casting Method and their Thermal Stability*

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A mostly single Al-based amorphous phase in a sheet form with a thickness of 0.2 mm was found to be formed in the composition range of 6 to 10 at% Ni and 4 to 6 at% Ce in Al-Ni-Ce system by a metallic mold casting process. With increasing sheet thickness, the as-cast structure changes to coexistent amorphous and crystalline phases in the sheets with thicknesses of 0.3 and 0.4 mm and crystalline phases in the sheet with a thickness of 0.5 mm. The composition range in which a mostly single amorphous phase is formed by casting is located at the Al-rich side against the $Al_{84}Ni_{10}Ce_6$ alloy with the widest supercooled liquid region. No amorphous single phase is formed for the alloys which are located at the Al-poor side, though the supercooled liquid region is observed. The deviation of the glass-formation range by casting from the composition range in which the supercooled liquid region is observed is presumably because of a high growth rate or an easy heterogeneous nucleation of eutectic-type crystalline phases which appear at the Al-poor concentration side. In addition, the application of the casting process to $Al_{84}Ni_8Y_8$ and $Al_{84}Ni_{10}La_6$ alloys caused the formation of coexistent amorphous and crystalline phases in the sheet with a thickness of 0.2 mm, presumably because of their lower glass-forming ability. The finding that the amorphous alloy sheet in the Al-based system is formed by the conventional casting process is quite important in the subsequent development of the amorphous alloys by utilizing the high mechanical strengths and good corrosion resistance.

KEYWORDS: aluminum-based alloy, amorphous phase, bulk alloy, mold casting method, large glass-forming ability

1. Introduction

Recently, Inoue et al. have found a series of new amorphous alloys in Ln-Al-TM [1,2], Mg-Ln-TM [3-5] and Zr-Al-TM [6,7] systems with large glass-forming ability and a wide supercooled liquid region before crystallization. Subsequently, the application of a metallic mold casting method to their alloys causes the formation of bulk amorphous alloys and the maximum thickness for formation of an amorphous phase reaches as large as 7 mm for the Ln-Al-Ni [8] and 4 mm for the Mg-Cu-Y [9] systems. In the previous study on the formation of bulk amorphous alloys by the metallic mold casting method, it has been reported [9] that the maximum thickness (t_m) is proportional to the temperature interval of the supercooled liquid region which is defined by the difference between T_g and T_x, $\Delta T_x(=T_x-T_g)$, e.g., t_m is about 1 mm for ΔT_x=20 K, 2.5 mm for ΔT_x=40 K and 4 mm for ΔT_x=60 K. It has previously been reported that Al-based amorphous alloys with high strength and good ductility have the ΔT_x values of about 20 K. The previous relation between ΔT_x and t_m allows us to expect that bulk amorphous alloys are also produced in Al-based alloys by the metallic mold casting method. Clarification of the possibility of producing bulk amorphous alloys in Al-based system by the metallic mold casting process is very important in the subsequent development of Al-based amorphous alloys. This paper is intended to present the structure and thermal stability of the bulk Al-based alloys produced by the metallic mold casting method and to determine the critical sample thickness for formation of an amorphous phase in Al-based alloys.

2. Experimental Procedure

Ternary alloys with alloy compositions of $Al_{84}Ni_8Y_8$, $Al_{84}Ni_{10}La_6$ and $Al_{84}Ni_{10}Ce_6$ were prepared by arc melting a mixture of pure Al, Ni, and Ln (Ln=Y, La or Ce) elements in an argon atmosphere. These ternary alloys were chosen because they had the largest supercooled liquid region before crystallization in each alloy system of Al-Ni-Y, Al-Ni-La and Al-Ni-Ce and were expected to have the largest glass-forming ability. In addition to the three alloys, ternary $Al_{100-x-y}Ni_xCe_y$ alloys were also used for the examination of the influence of the supercooled liquid region on the production of an amorphous sheet. From the master alloy ingot, thick sheet samples with a constant width of 5 mm and thicknesses of 0.1 to 0.5 mm were prepared by injection casting of the melt into copper molds with inner shapes of rectangular parallel-epiped. The schematic illus-

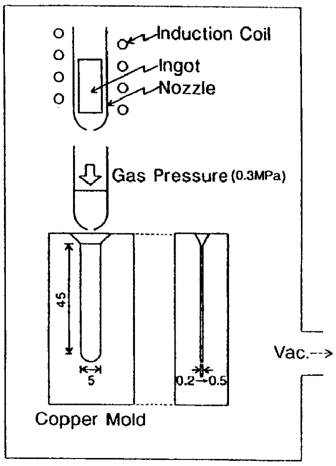

Fig. 1 Schematic illustration showing the present metallic mold casting method.

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tration of the equipment used in the present study is shown in Fig. 1. The injection pressure was fixed to be 0.3 MPa. For comparison, an amorphous ribbon with a cross section of about 0.02 x 1 mm^2 was also produced by the single roller melt spinning method in an argon atmosphere. The amorphicity of the as-cast samples was examined by X-ray diffractometry and optical microscopy (OM) techniques and differential scanning calorimetry (DSC). Hardness was measured under a load of 25 g with a Vickers microhardness tester.

3. Results and Discussion

Fig. 2 shows the X-ray diffraction patterns of the $Al_{84}Ni_{10}Ce_6$ sheets with thicknesses of 0.2, 0.3 and 0.4 mm, along with the data of the melt-spun ribbon with a thickness of 0.02 mm. The diffraction patterns taken from the surface and the inner central region of the sheet with a thickness of 0.2 mm consist only of a broad peak, indicating the formation of a mostly single amorphous phase. Even in the sheet sample with a thickness of 0.3 mm, the diffraction pattern consists mainly of a halo peak, though very weak peaks corresponding to Al and Al_4Ce are scarcely seen. However, the further increase in the sheet thickness to 0.4 mm causes the change into a crystalline structure consisting of Al, Al_4Ce and Al_3Ni phases and no any trace revealing the existence of an amorphous phase is seen. The peak position of the halo peak for the sheet with a thickness of 0.2 mm is measuered to be 26.0 nm^{-1}, in agreement with that (25.9nm $^{-1}$) for the melt-spun ribbon. It is therefore concluded that the metallic mold casting treatment causes the formation of an amorphous phase which is similar to that for the ribbon sample obtained by melt spinning. In addition, the critical sheet thickness for formation of an amorphous phase appears to lie in the range of 0.3 to 0.4 mm in the present metallic mold casting condition.

In order to confirm the formation of the amorphous phase, the DSC curves of the cast sheets with thicknesses of 0.2, 0.3, 0.4 and 0.5 mm are shown in Fig.3, where the data of the melt-spun ribbon are also shown for comparison. The glass transition temperature (T_g), the onset temperature of crystallization (T_x) and the heat of crystallization (ΔH_x) are 546 K, 563 K and 5.40 kJ/mol, respectively, for the amorphous sheet with a thickness of 0.2 mm. The T_g, T_x and ΔH_x values are nearly the same as those (543 K, 561 K and 5.31 kJ/mol) for the melt-spun ribbon, indicating that there is no distinct difference in the thermal stability between the cast amorphous sheet and the melt-spun amorphous ribbon. Furthermore, T_g, T_x and ΔH_x for the sheet with a thickness of 0.3 mm are also measured to be 547 K, 565 K and 4.74 kJ/mol and no distinct change in these properties is seen in comparison with those for the melt-spun amorphous ribbon and the amorphous sheet with a thickness of 0.2 mm, though the magnitude of the endothermic reaction due to the glass transition appears to decrease for the sheet with a thickness of 0.3 mm. The increase in the sheet thickness to 0.4 mm causes a drastic decrease in the heat of crystallization, accompanying the disappearance of the glass transition. These changes indicate that the as-cast structure consists of a mostly single amorphous phase for the sheet with t=0.3 mm and a mostly crystalline phase for the sheet with t=0.4 mm, being consistent with the result obtained by X-ray diffractometry.

In order to confirm the absence of any crystalliniety for the as-cast $Al_{84}Ni_{10}Ce_6$ sheet with a thickness of 0.2 mm as well as to examine the precipitation site of the crystalline phases for the as-cast sheets with thicknesses of 0.3 and 0.4 mm, the cross sectional structure of the cast sheets subject-

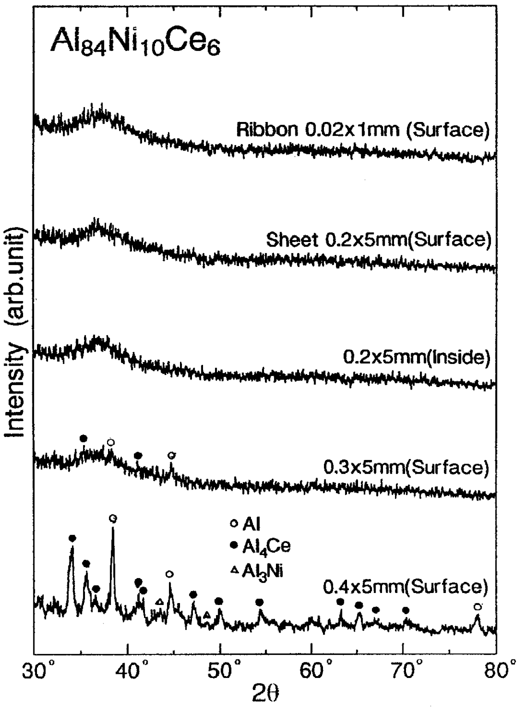

Fig. 2 X-ray diffraction patterns of as-cast $Al_{84}Ni_{10}Ce_6$ sheets with different thicknesses. The data of the melt-spun ribbon are also shown for comparison.

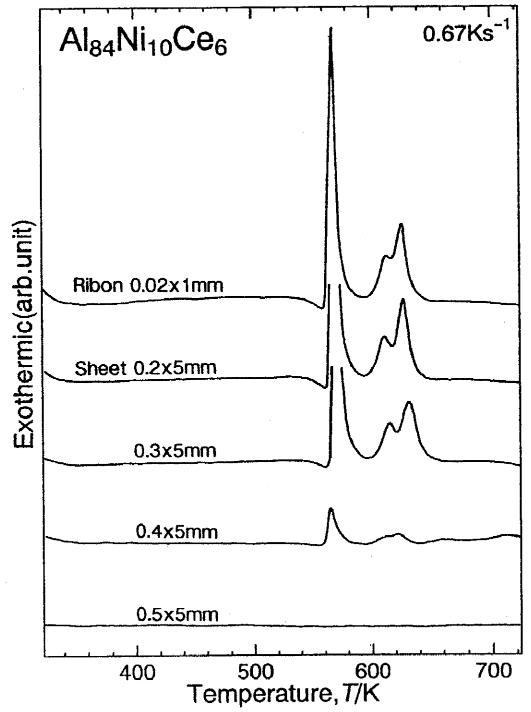

Fig. 3 DSC curves of as-cast $Al_{84}Ni_{10}Ce_6$ sheets with differrent thicknesses. The data of the melt-spun ribbon are also shown for comparison.

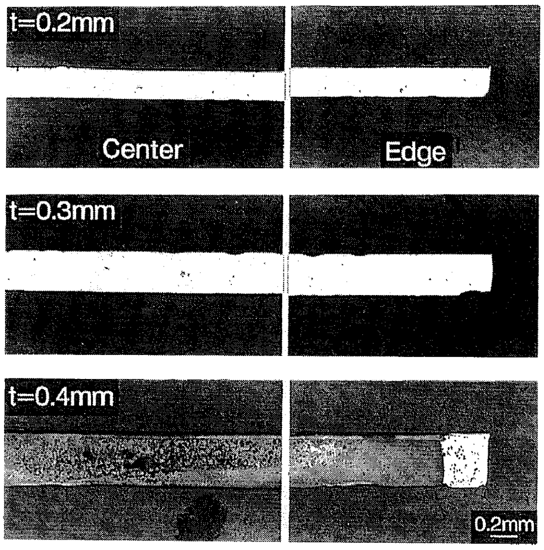

Fig. 4 Optical micrographs revealing the cross-sectional structure of as-cast $Al_{84}Ni_{10}Ce_6$ sheets with thicknesses of 0.2, 0.3 and 0.4 mm.

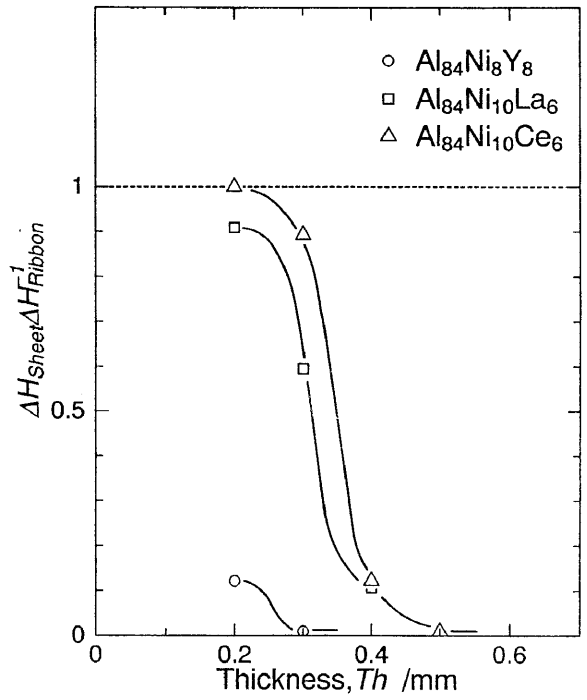

Fig. 5 The ratio of the heat of crystallization for an as-cast sheet to that for a melt-spun ribbon, $\Delta H_{sheet} / \Delta H_{ribbon}$, as a function of sheet thickness for $Al_{84}Ni_8Y_8$, $Al_{84}Ni_{10}La_6$ and $Al_{84}Ni_{10}Ce_6$ alloys.

ed to the etching treatment for 30 s at 298 K in NaOH solution is shown in Fig. 4. No distinct contrast revealing the precipitation of a crystalline phase is seen over the whole cross section for the sheets with thicknesses of 0.2 and 0.3 mm. For the sheet with a thickness of 0.4 mm, the crystalline phases of Al and compounds appear to precipitate along the direction of sample thickness. There is no tendency for the crystalline phase to precipitate preferentially in the central region of the cross section, though the cooling rate is thought to be the smallest in the central region which is the farther from the copper mold. The inconsistency is presumed to result from the easy precipitation of the Al and Al_4Ce phases which nucleate on the surface in a heterogeneous mode and grow simultaneously and cooperatively.

Fig. 5 shows the change with sample thickness in the ratio of the heat of crystallization for the sheet sample (ΔH_{sheet}) to that for the melt-spun ribbon (ΔH_{ribbon}) for the $Al_{84}Ni_8Y_8$, $Al_{84}Ni_{10}La_6$ and $Al_{84}Ni_{10}Ce_6$ alloys. The ratio is 1.0 for the Al-Ni-Ce sheet sample with t=0.2 mm where an amorphous single phase is formed. However, the ratio of ΔH_{sheet} / ΔH_{ribbon} is 0.12 for the Al-Ni-Y sheet with t=0.2 mm and 0.91 for the Al-Ni-La sheet with t=0.2 mm, indicating that no amorphous single phase is formed even in the thin sheet for the Al-Ni-Y and Al-Ni-La alloys. It is concluded that the glass-forming ability decreases in the order of Al-Ni-Ce > Al-Ni-La > Al-Ni-Y system. Considering that the temperature interval of the supercooled liquid region defined by the difference between T_g and T_x is 24 K for $Al_{84}Ni_8Y_8$, 17 K for $Al_{84}Ni_{10}La_6$ and 17K for

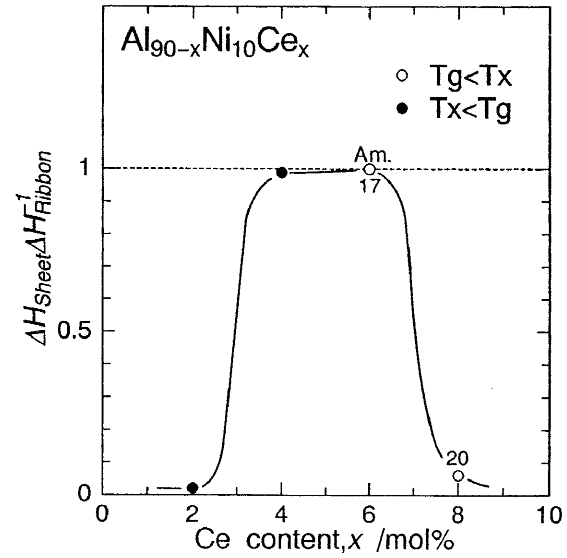

Fig. 6 The ratio, $\Delta H_{sheet} / \Delta H_{ribbon}$ as a function of Ce content for as-cast $Al_{90-x}Ni_{10}Ce_x$ sheets with a thickness of 0.2mm.

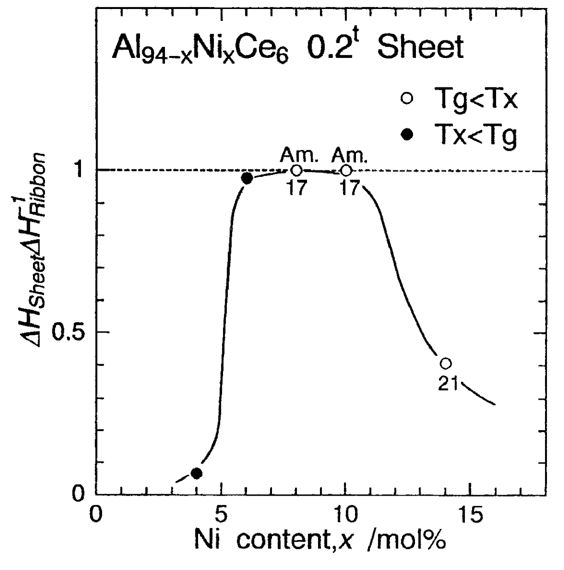

Fig. 7 The ratio, $\Delta H_{sheet} / \Delta H_{ribbon}$ as a function of Ni content for as-cast $Al_{94-x}Ni_xCe_6$ sheets with a thickness of 0.2 mm.

$Al_{84}Ni_{10}Ce_6$, it seems that the glass-forming ability does not always reflect the temperature interval of the supercooled liquid region.

It is therefore expected that a similar amorphous sheet with a thickness of 0.2 mm is obtained in Al-Ni-Ce alloys with other compositions, even though the supercooled liquid region is smaller. Figs. 6 and 7 show the change in ΔH_{sheet} / ΔH_{ribbon} as a function of Ce and Ni content for as-cast $Al_{90-x}Ni_{10}Ce_x$ and $Al_{94-x}Ni_xCe_6$ sheets with a thickness of 0.2 mm, along with the data of the temperature interval of the supercooled liquid region. It is seen that a mostly single amorphous phase is formed for the $Al_{86}Ni_{10}Ce_4$, $Al_{88}Ni_6Ce_6$ and $Al_{86}Ni_8Ce_6$ sheets, in addition to the $Al_{84}Ni_{10}Ce_6$ sheet. Here, it is to be noticed that the amorphous sheet is obtained in $Al_{86}Ni_{10}Ce_4$ and $Al_{88}Ni_6Ce_6$ alloys without appreciable glass transition. On the contrary, the $Al_{82}Ni_{10}Ce_8$ and $Al_{80}Ni_{14}Ce_6$ alloys with the large ΔT_x values of 20 and 21K consist mainly of crystalline phases. This result indicates that the extension of the supercooled liquid by the dissolution of a large amount of solute elements is not effective for the production of an amorphous sheet by the present metallic mold casting process. This result is inconsistent with the expectation from the temperature interval of the supercooled liquid region reflecting the stability of the supercooled liquid. The inconsistency is presumably due to heterogeneous nucleation in the present casting process and high growth rate for the polymorphic crystallization of Al and compound which occurs in a high solute concentration range. On the other hand, the crystallization of the Al-based amorphous alloys with solute concentrations below 15 at% takes place through two stages of Al → Am+fcc-Al → Al+compound and the growth of the primary Al phase has been reported[11] to be much slower than that for the polymorphic Al and compound.

The Vickers hardness number of the as-cast sheet with a thickness of 0.2 mm is 342 for $Al_{86}Ni_8Ce_6$ and 386 for $Al_{84}Ni_{10}Ce_6$, being slightly higher than those (298 and 350) for the corresponding melt-spun ribbons, respectively. The slight increase in Hv seems to be attributed to the progress of the structural relaxation for the cast samples because of their low cooling rates.

In any event, the information that a mostly single amorphous phase in Al-Ni-Ce system is formed in the sheet form with thicknesses below 0.3 mm by the metallic mold casting method is very important in the subsequent development of Al-based amorphous alloys which have been reported to have high mechanical strength and good corrosion resistance.

4. Summary

The application of a metallic mold casting process to Al-Ni-Ce alloys containing 6 to 10 %Ni and 4 to 6 %Ce was found to cause mostly single amorphous sheets with a thickness of 0.2 mm. The further increase in the sheet thickness results in the formation of mixed amorphous and crystalline phases. However, no amorphous single phase is formed in the cast $Al_{84}Ni_{10}La_6$ and $Al_{84}Ni_8Y_8$ sheets with a thickness of 0.2 mm. The composition range in which the mostly single amorphous sheet with a thickness of 0.2 mm is obtained deviates to the Al-rich side from the composition range where the supercooled liquid region is observed before crystallization. The deviation is presumably due to the high growth rate of eutectic-type Al and compound phases which appear at the compositions with a wide supercooled liquid region. The production of Al-based amorphous sheets by the conventional casting process is very important in the subsequent progress of Al-based amorphous alloys with high mechanical strengths and good corrosion resistance.

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