Effect of Ceramics Addition on Formation Tendency of Amorphous Phase in $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ Alloy[†]

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The effect of additional ceramic powder on the formation tendency of an amorphous phase in a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy was investigated by water quenching of a molten alloy. The specimens were 12 mm in diameter and 6 mm thick. In the alloy without ceramic powder, the amorphous phase forms only near the surface of the specimen. By the addition of 6 vol% TiB_2 powder, it was possible to produce a homogeneous alloy specimen with amorphous and crystalline phases. In order to analyze the role played by ceramic powder in this process, various kinds of ceramic powders were added. TiC powder played the same role as TiB_2 powder in this process, but TiN and ZrB_2 powders did not. A crystalline phase about 20 μm in thickness was observed at the surface of TiB_2 in the optical microstructure. By EPMA, this crystalline phase was confirmed to have a composition of poorer La and richer Al, Ni than the matrix phase. Since the crystal preferentially nucleate at TiB_2 surface and grows slowly, the matrix phase would easily form an amorphous state.

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I. Introduction

La-Al-Ni system alloys have high glass forming ability⁽¹⁾. A $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy has the critical cooling rate of 100 K/s⁽²⁾⁽³⁾, and this enables us to obtain an amorphous phase by water quenching⁽²⁾. If a bulk amorphous alloy is prepared by water quenching, it is expected to extend commercial applications of amorphous alloys.

In the previous study, we succeeded in preparing an amorphous $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy by a newly devised water quenching method⁽⁴⁾. By incorporating TiB_2 powder into a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy, the glass forming ability of this alloy was improved and amorphous and crystalline phases were dispersed homogeneously in the whole region of specimen. Therefore, this method is effective for preparing bulk amorphous alloys. Understanding the mechanism of this effect is important to apply for a practical alloy system.

In this study, rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ composite materials with ceramic powders of TiB_2 , TiC , TiN , TiO_2 and ZrB_2 are prepared, and the effects of each ceramics on the glass forming ability of the alloy are investigated. Furthermore, a rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy on a TiB_2 plate is prepared in order to observe the microstructure of the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}/\text{TiB}_2$ interface. On the basis of these results, the effects of ceramic powders on the formation tendency of an amorphous phase in a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy are investigated.

II. Experimental

1. Preparation of rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy-ceramic powder composites

According to the process A in Fig. 1, rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy-ceramic powder composites were prepared. Starting materials of the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy were La lump (99.9 mass% purity), Al chip (99.99 mass% purity) and Ni powder (99 mass% purity). TiB_2 , TiC , TiN , TiO_2 and ZrB_2 powders 10 to 20 μm in particle size were used for additional ceramic. Ceramic powders of 6 vol% were added to 4 g of a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy. These materials were melted in a carbon crucible by a high frequency induction furnace under Ar gas flow. The carbon crucible was coated with BN powder to prevent the reaction be-

Fig. 1 Preparation of rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy specimens.

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tween a molten material and a crucible. A water-cooled copper block was pushed into the crucible. The molten alloy was solidified and shaped into a cylindrical form 12 mm in diameter. The obtained specimen was placed on a carbon plate coated with BN and reheated in a high frequency induction furnace under an Ar gas flow. It was held at 1000 K for 300 s and then quenched in water. According to thermal analysis by DSC, the liquidus line of this alloy was 870 K. Therefore, the superheat of the specimen in this process was more than 100 K. Then, the cylindrical specimen was scarcely deformed at the temperature (1000 K) over the liquidus line, because an oxide film formed on the specimen surface retains the original cylindrical shape. The oxide film on the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy was sufficiently unreactive to BN, so the specimen was removed from the carbon plate and then cooled well with water from overall surface. Moreover, the effects of TiC, TiN, TiO_2 and ZrB_2 additions on the formation tendency of an amorphous phase in a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy were compared with that of TiB_2 addition. The particle sizes of these ceramic powders were 10 to 20 μm to avoid cohesion of ceramic powder in the molten alloy. The cross-sectional microstructure of the specimen was observed after 2% nital etching.

2. Preparation of the specimen to examine an interface between a rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy and a TiB_2 plate

According to the process C in Fig. 1, the specimen to examine an interface between a rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy and a TiB_2 plate was prepared. A preformed $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy cylindrical specimen, 12 mm in diameter and 6 mm in thickness, was prepared in the same way as described in Section II-1. The TiB_2 plate was made by sintering of pure TiB_2 powder, 0.9 μm in particle size, at 1923 K under a pressure of 50 MPa using a spark plasma sintering system (SPS-510L made by Sumitomo Coal Mining Co. Ltd.). The size of the TiB_2 plate was 15 mm in diameter and 4 mm in thickness, and its porosity was about 20 vol%. On the preformed $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy specimen, an oxide film on the surface which would be in contact with the TiB_2 plate was removed by polishing with emery paper and 3 μm diamond particles. Furthermore, the polished surface was cleaned by an ultrasonic cleaning equipment. The TiB_2 plate was also polished in the same way. The $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy specimen was placed on the TiB_2 plate, kept at 1000 K for 300 s in a high frequency induction furnace under Ar gas flowing, and quenched in water. For comparison, the rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy specimen with a Ti plate

Fig. 2 Vertical sectional view of a rapidly solidified specimen.

was also prepared by the process shown in Fig. 1B. The cross-sectional microstructure of these specimens was observed after 2% nital etching and analyzed by EPMA.

III. Results

1. Effect of various ceramic powder addition on the formation tendency of an amorphous phase in a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy

Rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ composite materials with ceramic powders of TiB_2 , TiC, TiN, TiO_2 and ZrB_2 were prepared, and effect of each ceramics on the glass forming ability of the alloy was investigated. In this study, an image processing method is effective in analyzing a dispersed amorphous phase. Optical refractivity of an amorphous phase becomes higher than that of a crystalline phase in the polished surface after etching. The amorphous area was measured along the central axis on the cross-sectional view of the cylindrical specimen. The unit area for the image processing analysis was 0.8 mm $\times$ 0.8 mm, and was measured continuously every 0.2 or 0.4 mm step in d -direction as shown in Fig. 2. Figures 3 and 4 show the distribution of the amorphous phase in d -direction of the cylindrical alloy specimens. The horizontal axis shows the distance from the top surface to each measuring point and the vertical axis shows the area fraction of the amorphous phase. Table 1 shows the average fraction of the amorphous phase in the image processing analyzed area for each specimen. Figure 5 shows the cross-sectional microstructures at the center of each specimen.

In the alloy specimen without ceramic powder, the region near the surface is almost amorphous. However, the phase drastically changes 1 to 2 mm in the distance from the surface. The amorphous phase rapidly decreases with increasing the distance from the surface, and the crystalline phase is dominant in the central region. In the composite material containing 6 vol% of TiB_2 powder, the fraction of the amorphous area gradual-

Fig. 3 Effect of the addition of titanium compound powders on the distribution of the amorphous phase in the vertical section of specimens. d shows the distance from the top of the disk specimen.

ly decreases with increasing the distance from the surface, and has lower fraction in the vicinity of the surface part. However, it is rather stressed here that the fraction

Fig. 4 Effect of the addition of boride powder on the distribution of the amorphous phase in the vertical section of specimens. d shows the distance from the top of the disk specimen.

Table 1 Average fraction of the amorphous phase in the image processing analyzed area.

Added powder	None	TiB ₂	TiC	TiN	TiO ₂	ZrB ₂
Average fraction of amorphous phase (%)	50	64	80	21	0	17

of the amorphous area becomes more than 50% in the central part of the specimen. As shown in Table 1, average fraction of the amorphous phase in the alloy specimen with TiB₂ powder is higher than that without ceramics powder. Addition of TiC powder also causes same effect in the case of TiB₂ powder as shown in Figs. 3 and 5. Average fraction of the amorphous phase in the specimen with TiC powder is also higher as shown in Table 1.

Additions of TiN and ZrB₂ powders were not effective in the formation of an amorphous phase as shown in Figs. 3, 4, 5 and Table 1. TiN and ZrB₂ powders were more difficult to disperse in the La₅₅Al₂₅Ni₂₀ alloy than

Fig. 5 Microstructures of rapidly solidified a La₅₅Al₂₅Ni₂₀ alloy containing different ceramic powders.

TiB_2 and TiC powders. The wettability of the molten $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy on TiN and ZrB_2 surfaces may be low.

The $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy specimen with TiO_2 powder was different in microstructure from the other composite specimens, showing no amorphous phase as shown in Fig. 5. This specimen was a gray needle-like crystal. This type of crystal was observed also in the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy specimen with Al_2O_3 powder, it was identified to be La_2O_3 by EPMA. TiO_2 and Al_2O_3 acted as an oxygen donor by decomposing in a molten alloy and La was oxidized. As a result, the composition of this alloy changed and the glass forming ability was lowered.

2. Observation of the microstructure at the interface between the rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy and the TiB_2 plate interface

Figure 6 shows the photographs and schematic illustrations of the cross-sectional view of the rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy specimens. Specimens A, B and C were remelted and water quenched on a BN coated carbon plate, on a titanium plate and on a TiB_2 plate, respectively. Specimens B and C were somewhat deformed during the remelting process, because the oxide film on the surface attached to the Ti and TiB_2 plates had been removed. The oxide film on the specimen A had not been removed before remelting. BN was stable for the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy to 1000 K. The BN-coated carbon plate was sufficiently unreactive to an alloy specimen during the remelting process, so that the alloy specimen A was easy to remove from the plate at the water quenching process and efficiently cooled from the overall surface. As a result, the amorphous phase existed only in the vicinity of the surface and the crystalline phase existed in the

central region of the sample (specimen A). This is the typical distribution of amorphous and crystalline phases in the rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy. In the case of the specimen B, although a titanium plate was unreactive chemically to the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy, the alloy specimen and the titanium plate did not separate because the oxide film on the surface attached to the plate. So the amorphous phase existed only in the vicinity of the top and side surfaces which were cooled directly with water, and the crystalline phase existed from the bottom interface to the central region because of the lower cooling rate for the titanium plate. In the case of the specimen C, although a TiB_2 plate was unreactive to a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy, the alloy specimen and the TiB_2 plate did not separate same as the case of the specimen B. However, the distribution of amorphous and crystalline phases in the specimen C was different from that in the specimen B. The border between amorphous and crystalline phases in the specimen C was of the same arc shape as the specimen B. The cooling rate of the alloy specimen on the TiB_2 plate became lower than the critical cooling rate to form an amorphous phase, as is the case with the titanium plate. However, there was an amorphous phase near the TiB_2 plate in the specimen C. That is to say, TiB_2 might contribute to form an amorphous phase in the vicinity of the surface of an alloy.

IV. Discussion

By incorporating TiB_2 or TiC powder into a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy, the glass forming ability of the alloy was improved and amorphous and crystalline phases were dispersed homogeneously in a whole of specimen. It is possible to make a few predictions about causes of such phenomena.

(1) The cooling rate of an alloy specimen becomes higher.

(2) The alloy composition changes by the reaction of added ceramics.

(3) The solidification process of an alloy changes by growing an anomalous crystalline phase from the ceramics-added surface.

The effect of ceramics addition on the formation tendency of an amorphous phase in a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy will be discussed from these three points of view.

1. Cooling rate

Table 2 shows thermal conductivities, K , of TiB_2 , TiC , TiN , and ZrB_2 ⁽⁵⁾. The thermal conductivity of TiC was lower than the others. So, addition of TiC was most dis-

Fig. 6 Microstructures and schematic illustrations of vertical sections of the rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy disks. Specimens A, B and C were remelted and water quenched on a BN coated carbon disk, a titanium disk and a TiB_2 disk, respectively.

Table 2 Thermal conductivities of some ceramics⁽⁵⁾.

	Thermal conductivity, $K/\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$
TiB_2	69.9 (1300 K)
TiC	30.0 (1773 K)
TiN	67.8 (1773 K)
ZrB_2	64.5 (1300 K)

Table 3 Densities and specific heats at 1000 K of some ceramics⁽⁵⁾.

	Density, $\rho/\text{g cm}^{-3}$	Specific heat, $c_p/\text{J g}^{-1} \text{K}^{-1}$	$\rho c_p/\text{J cm}^{-3} \text{K}^{-1}$
TiB ₂	4.53	1.126	5.10
TiC	4.92	0.858	4.22
TiN	5.44	0.849	4.62
ZrB ₂	6.09	0.658	4.01

advantageous for amorphous formation from the viewpoint of a cooling rate. However, it was actually effective for amorphous formation. The heat capacity also must be compared when the cooling rate of material is considered. Since the added ceramic powders were 6 vol% in all the specimens prepared in this study, the heat capacities can be compared by using products of densities, ρ , and specific heats, c_p . As shown in Table 3⁽⁵⁾, the difference in the value of ρc_p among each ceramics does not seem to be significant. From these data, there is no correlation between the amorphous formation tendency and the thermal character of the added ceramics powder.

2. Alloy composition

Generally, a glass forming ability of an alloy becomes higher with increasing variety of alloying elements. In the case of a La–Al–TM alloy, for example, the glass forming ability increases in the sequence of $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20} < \text{La}_{55}\text{Al}_{25}\text{Ni}_{10}\text{Cu}_{10} < \text{La}_{55}\text{Al}_{25}\text{Cu}_{10}\text{Ni}_5\text{Co}_5$ ⁽³⁾. On the other hand, adding 1 to 2 at% of light elements, beryllium, boron or carbon, increase the glass forming ability of the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy drastically⁽⁶⁾. Therefore, if boron dissolve from the TiB₂ into the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy, it

will cause the improvement of the glass forming ability. In the matrix of the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy, boron was not detected by wave dispersive X-ray spectroscopy (WDX). However, the sensitivity for boron by WDX is only about 1%, and is insufficient to analyze minute amounts of boron. Therefore, we will make the following discussion.

If TiB₂ decomposes in a molten $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy and boron dissolves, the following two reactions can be expected:

If the reaction (1) occurs, the ratio of titanium to boron (Ti/B) at the reacted region in TiB₂ must be different from that at the unreacted region. The $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy penetrate into the surface of the TiB₂ plate as shown in Fig. 6C. The Ti/B ratio in the TiB₂ plate which was penetrated by the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy was almost the same as the other region in TiB₂. Though the absolute sensitivity for boron on WDX is poor, it is sufficient to detect the difference of the Ti/B value between TiB and TiB₂. Accordingly, the reaction (1) may not occur. If the reaction (2) occurs, titanium as well as boron must dissolve into the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy phase. However, titanium was not detected in the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy phase on WDX. Therefore, the reaction (2) may not occur.

3. Solidification mechanism

As shown in Fig. 7, 10 to 20 μm crystals grew on the surface of TiB₂, and the around region of this crystal was an amorphous phase. Figure 8 shows the EPMA at the

Fig. 7 Microstructures of the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}/\text{TiB}_2$ interface and of the center part of $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ in a rapidly solidified specimen.

Fig. 8 EPMA at the interface of $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}/\text{TiB}_2$ in a rapidly solidified specimen.

interface between the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy and TiB_2 plate in the rapidly solidified specimen. The chemical composition of the crystal on the TiB_2 plate was different from that of the amorphous phase; the former was $\text{La}_{40}\text{Al}_{30}\text{Ni}_{30}$ and the latter was $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$. On the other hand, the composition of the crystalline phase in the central region of the alloy specimen was almost the same as the amorphous phase. Therefore, the crystal on TiB_2 is different from the crystal in the central region. Concentrating of Al and Ni on the TiB_2 surface may be caused by the difference in affinity of La, Al and Ni to TiB_2 . Al and Ni, which have stronger affinity to TiB_2 than La, were concentrated in the crystal on the TiB_2 surface. Since the concentration of La was low in the crystal on TiB_2 , La was concentrated around the crystal. The concentrated La must diffuse into the matrix phase for growth of the crystal on TiB_2 . However, this crystal growth may be suppressed because of the small diffusion rate of La⁽⁷⁾. In addition, a homogeneous nucleation is suppressed, because an inhomogeneous nucleation on the TiB_2 surface predominates. As a result, the structure of the “ TiB_2 /thin crystalline phase/amorphous phase”

forms and suppresses the crystallization in the alloy matrix phase. TiB_2 and TiC powders were easier to disperse in a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy than TiN and ZrB_2 powders. This means that the wettability of a molten $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy on TiB_2 and TiC surfaces are good. An interfacial character between metal and ceramics corresponds to several phenomena observed in this study.

V. Conclusions

- (1) Incorporation of TiB_2 or TiC powder into a $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy is effective for amorphous formation, but that of TiN or ZrB_2 accelerates crystallization.
- (2) Incorporation of TiO_2 or Al_2O_3 , which decomposes in a molten $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy, accelerates crystallization.
- (3) In the rapidly solidified $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy specimen on a TiB_2 plate, the thin crystalline phase which has richer Al and Ni than the matrix phase grows on the TiB_2 surface. An inhomogeneous nucleation on the TiB_2 surface preferentially occurs and the growth rate of the thin crystal is slow. For this reason, the amorphous forma-

tion in the matrix phase around the crystalline phase on TiB_2 is accelerated.

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