LETTERS TO THE EDITOR

Reply to Comments by Tsuyoshi Kajitani on Our Paper Titled ‘Production of $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_{5}\text{Al}_{10}$ Glassy Alloy Rod of 30 mm in Diameter by a Cap-Cast Technique (by Y. Yokoyama, et al., Mater. Trans. 48 (2007) 3190–3192)’

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Our paper (Mater. Trans. 48 (2007) 3190–3192) reports (1) the importance of controlling the impurity oxygen content during the manufacture of $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_{5}\text{Al}_{10}$ bulk metallic glasses (BMGs) and (2) the successful fabrication of a BMG rod of 30 mm diameter rod by our newly developed ‘cap casting’ technique. In response to Kajitani’s comments, where he questions the validity of the proposed method through his eight specific criticisms, we have made our assertion from an academic viewpoint. He has rightly pointed out a typographical error, where the TEM apparatus has been typed as JEOL 4000 FX instead of JEM-4000EX, for which we apologize. Nevertheless, our TEM, JEM-4000EX has indeed better resolution than that of ‘FX’ and, thus, this typographical error does not diminish the scientific significance of our results.

Below are our detailed responses to Kajitani’s eight specific comments.

Reply to comment 1: Thermal analysis of the master alloy button was carried out by DSC (differential scanning calorimetry) at the experimental stage. Figure 1 shows the DSC curve taken from the vitrified region of the $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_{5}\text{Al}_{10}$ master alloy button shown in Fig. 4 in our 2007 paper. As you can see, there are clear endothermic and exothermic heats at $T_g = 689$ K and $T_x = 774$ K, respectively. However, since one of the objectives of our 2007 study was to estimate the difference in the glass-forming ability between $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_{5}\text{Al}_{10}$ master alloys with different Zr purities, the optical micrograph was shown in Fig. 2 instead of the DSC data in that paper. The micrograph clearly shows that crystalline inclusions are present in the low-purity alloy and not in the high-purity alloy.

Reply to comment 2: Vitrification can be achieved in the supercooled liquid only when the freezing rate (the moving speed of the isothermal plane during glass transition) exceeds the crystal growth rate. Therefore, vitrification would be suppressed if the crystal growth rate is sufficiently high and a large number of nuclei are formed in the supercooled liquid during solidification.

Kajitani states that ‘the authors indicate that slow cooling of the low-oxygen samples is a key factor for obtaining the amorphous state’. However, we believe that there has been some misunderstanding from his side. The aforementioned theory is incorrect, and further, we have made no such statement in our paper. Needless to say, ‘The higher the cooling rate, the higher is the degree of vitrification’.

Kajitani is probably confused with two separate issues addressed in our paper: (a) the slow cooling of the top surface of the small master alloy button (weight: $\sim 25$ g; diameter: 26 mm; height: 10 mm) and (b) rapid cooling of the larger BMG rods because of the use of the ‘cap casting’ method. During the (a) fabrication of the master alloy, crystalline nuclei may be generated at the contact plane between the molten alloy and the Cu hearth, and this may result in partial crystallization, even though the cooling rate at the bottom side of the ingot is high. On the other hand, the top portion of the ingot melts thoroughly during arc melting, and hence, vitrification occurs even though the cooling rate in this region is slower than that in the bottom surface. It has been experimentally proved that the bottom surface (where the cooling rate is higher than that in the vitrified top surface) of the arc-melted $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_{5}\text{Al}_{10}$ master alloy button may include a crystallized region. The cap cast technique is advantageous for (b) BMG formation, as it helps to enhance the cooling rate in the top portion of the specimen; this is because the Cu cap on the upper surface of the specimen suppresses undesired crystallization in this region.

Therefore, there is no contradiction in our paper, and Kajitani’s statement ‘There appears to be a contradiction’, is simply false and unjust.

Reply to comment 3: Kajitani has stated that ‘Within the best knowledge, however, such large amount of master alloy cannot be melted by a conventional arc-melting machine’. This statement is simply false and unjust. As you can see, there are clear endothermic and exothermic heats at $T_g = 689$ K and $T_x = 774$ K, respectively. Therefore, there is no contradiction in our paper, and Kajitani’s statement is simply false and unjust.
An arc-melting system with a melting capacity of 200 g has been commercially available since 2002 from Nisshin Giken Inc. (Model: NEV-IHC200), and its photograph is shown in Fig. 2 with some pertinent specifications. This machine (NEV-IHC200) has been designed using the information provided in a patent published by a member of our research group (Y. Yokoyama). This system has been used since then in various studies, including the present research. This system has also been used since 2006 by many researchers throughout Japan who participated of the ‘Nationwide research collaboration program’. Since this system is well known to most researchers, we feel that Kajitani’s statement ‘Neither were details given regarding the essential specifications of the arc-melting machine for the cap-cast method’ is not justified.

We fabricated alloy buttons weighing less than 30 g in order to ensure the best homogeneity during in arc melting and carried out melting with utmost care to allow complete melting of the alloy. To ensure homogeneity, we flipped the alloy button over and continued the melting process. We repeated this process for more than four times; however, with the Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ alloy, it was easy to achieve homogeneity during arc melting, because of the properties of the alloy mentioned in the previous comment. We also found that it is important to maintain a low oxygen content in the alloy during arc melting.

To ensure complete melting before casting, we carried out arc heating in two steps: (1) melting all the master alloy buttons together and (2) further melting of the molten alloy just at the pouring gate, as has been described in our earlier papers (Refs. 7 and 8).

Another of Kajitani’s statement ‘A large temperature gradient, exceeding 10^6 K/m, is expected from the top to the bottom...’ is also baseless. From the pyrometer measurements made during the arc-melting process, we estimated the temperature gradient to be less than 110 K/mm, a value 10 times smaller than that stated by Kajitani. Furthermore, since we were familiar with the arc-melting method, we have taken care to address every possible issue that could arise when using this method.

Reply to comment 4: Kajitani claims that ‘The melt-quenching of arc-melted ingots into the water-cooled mold may have resulted in a less-homogeneous products. It is hardly conceivable that homogeneous glassy alloy rods can be directly cast by the arc-melting on water cooled copper hearth’. It appears that Kajitani is not familiar with the advancements in research and development in the last 10 years.

We also found that the properties of the Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ alloy make it suitable for arc melting, such as low melting temperature (1163 K), high viscosity in the molten state, and large wetting angle with the Cu hearth. These advantageous properties of the Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ alloy allow us to achieve a well-defined melting state with relative ease, even by the conventional arc-melting method.

Reply to comment 5: At the time of publication of the paper (July 2007), we did not have a stereoscope for observing the sample with a diameter of 30 mm; however, with our then-available equipment, we could carry out observations of the sample with 20 mm diameter. Therefore, we used a conventional technique, composite photography, to obtain four segmented images, which we combined to reconstruct the complete image. Figure 3 in this paper shows the image of the same cross-sectional BMG specimen recorded using our recently acquired stereoscope camera with wide field of view. The simple fact that Fig. 4 in our paper shows straight-line boundaries of individual photographs confirms that we have fabricated alloy buttons weighing less than 30 g in order to ensure the best homogeneity during in arc melting and carried out melting with utmost care to allow complete melting of the alloy. To ensure homogeneity, we flipped the alloy button over and continued the melting process. We repeated this process for more than four times; however, with the Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ alloy, it was easy to achieve homogeneity during arc melting, because of the properties of the alloy mentioned in the previous comment. We also found that it is important to maintain a low oxygen content in the alloy during arc melting.

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not attempted to manipulate the original images, which we could have done had we intended to.

Reply to comment 6: Kajitani has rightly stated that ‘JEM-4000FX machine has not existed since 1990 in the Institute of Materials Research...JEM-4000EX machine was in use. The authors should be careful for their documentation’. We thank Kajitani for pointing out the error in our typing. However, JEM-4000EX and FX are basically the same, as both are equipped with a LaB₆ electron gun, and that JEM-4000FX has better analytical capacity, although its resolution is slightly lesser. Therefore, this typographical error does not affect conclusions reported in our paper. Nevertheless, we apologize for this error. In addition, the sample thickness in the thin region of the TEM sample is estimated as approximately 10–30 nm.

Reply to comment 7: We have confirmed that the HRTEM image recorded by a scanner (1200 dpi) from the printed journal page (not from the PDF file available on the JIM website) reveals a random maze-like structure, which confirms the amorphous nature of the alloy. We are aware that PDF files downloaded from Internet websites are not always technically accurate because of their limited data size.

Reply to comment 8: This is a Rapid Publication and not a Review. In this paper, we (1) report the importance of the purity of the master alloy, particularly the impurity oxygen content, in producing vitrified master alloy buttons and (2) introduce a new ‘cap casting’ technique and demonstrate its feasibility for producing large-size BMG rods.

The suction casting method developed by our research group in 1996 was successfully used to produce BMG rods with 30 mm diameter; however, it had several disadvantages (difficulty in demoulding, generation of cast defects, etc.) that limited its practical applicability. These difficulties have been overcome in our new ‘cap casting’ technique, which is suitable for producing large-size BMGs. This is confirmed from the reported result, according to which the diameter of the cap-cast Zr₅₅Cu₃₀Ni₅Al₁₀ BMG rod (30 mm) well exceeds the critical diameters (16 and 20 mm) obtained in injection casting and tilt casting, which have been referred to as ‘conventional metallic mold cast technique’ and ‘conventional cast technique’, respectively, in our 2007 paper.

To conclude, we emphasize that there is no internal contradiction whatsoever in our paper and that those who are interested in the details of our equipment can obtain them from the vender.