Comments on the Paper “Production of Zr$_{55}$Cu$_{30}$Ni$_5$Al$_{10}$ Glassy Alloy Rod of 30 mm in Diameter by a Cap-Cast Technique”
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The authors of the title paper under discussion state the importance of low oxygen content in producing an amorphous top half in slowly cooled arc-melted buttons. Since the cooling rate does not favor the amorphous state in top half of the button, more evidence is needed to support the claim. Further, the authors made a liquid quenching machine to enhance the cooling speed to make larger ingots of the same alloy. It is not clear why a new machine with higher cooling rate is needed if the amorphous state can be achieved at lower cooling rates. Lack of essential details of the “cap-cast method” does not permit a critical assessment of the new process. The nature and quality of optical micrographs and HREM pictures are a cause of concern. [doi:10.2320/matertrans.M2009156]

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1. Summary of the Title Paper

This paper describes a new casting technique and the required oxygen level for successful production of Zr$_{55}$Cu$_{30}$Ni$_5$Al$_{10}$ glassy alloy rod up to 30 mm in diameter. The casting technique named “cap-cast method” consisted of arc-melting the alloy followed by quick casting into water cooled copper mold; a copper “cap” is used to compress the alloy melt at 1 kN from the top surface immediately after casting. This cap is needed to prevent shrinkage cavity and to enhance the cooling speed of the alloy melt. Low oxygen level, less than 45 mass ppm in the starting zirconium metal, was required to obtain homogeneous Zr$_{55}$Cu$_{30}$Ni$_5$Al$_{10}$ glassy alloy rod. Otherwise, crystalline inclusions were observed in the glass matrix. It is also stated that “the formation of a single glassy phase in the half topside of master alloy” was confirmed for the as-arc melted button ingots, cooled naturally on the copper hearth.

It is concluded that (1) the purity level of alloy component is an important factor to produce glassy alloy rods with large size and (2) the Zr$_{55}$Cu$_{30}$Ni$_5$Al$_{10}$ glassy alloy rods of up to 30 mm in diameter could be produced by means of the cap-cast technique; the critical size of glassy alloy rods is 20 mm by the conventional cast technique using copper molds.

2. Critical Comments Concerning the Title Paper

(1) Enough evidence, e.g. DSC or DTA curves showing the glass transition temperature, $T_g$, and crystallization temperature, $T_x$, is not given. Nevertheless, the authors state that the amorphous layer covers the half topside of the arc-melted alloy buttons.

(2) Along with the cooling speed, the importance of oxygen content (less than 45 mass ppm) for the starting zirconium metal was identified as an essential factor for the stability of the amorphous layer. Since the topside of the arc-melted buttons was slowly cooled compared to the bottom, which was directly contacting the copper hearth, the crystalline state is quite likely realized there. On the one hand, the authors of the title paper state that the “cooling speed in the melt-quenching procedures was the most important factor” and the cap-cast method was designed to realize “rapid cooling”. On the other hand, the authors indicate that slow cooling of the low-oxygen samples is a key factor for obtaining the amorphous state. There appears to be a contradiction. If amorphous state can be achieved by slow cooling of low-oxygen samples, the cap-cast method would not be needed for the production of glassy alloy rods!

(3) The cap-cast method was not explained clearly. For production of glassy alloy rods, e.g. $30 \text{ mm} \times 30 \text{ mm}$ in size, about 144 g of master alloy are required. To the best knowledge of the present author, such large amount of master alloy cannot be melted by a conventional arc-melting apparatus. A machine with at least four times higher power is needed. Maximum power requirement could exceed 40 kW. Homogenization of the 144 g sample would have been a very difficult task. Cooling water requirement would have been formidable. In the conventional equipment, 20 litters of cooled water are needed per minute to prevent melting of the copper hearth on which samples are arc-melted. A lot more water would have been needed for the cap-cast machine. Neither were details given regarding the essential specifications of the arc-melting machine for the cap-cast method and the homogenization process for ingots, nor references provided to source information.

(4) The arc-melting method is very useful for making small metal ingots, typically 25 g, consisting of refractory and/or transition metals. A major shortcoming of this method is the in-homogeneity of the product. A large temperature gradient, exceeding $10^6 \text{ K/m}$, is expected from the top to the bottom of the alloy melt during
melting, since the top layers are heated by the argon plasma and the bottom layers touch water-cooled copper hearth. The melt-quenching of arc-melted ingots into the water-cooled mold may have resulted in a less-homogeneous product. It is hardly conceivable that homogenous glassy alloy rods can be directly cast by arc-melting on water cooled copper hearth.

(5) Figure 3(b) and Figure 4(b) of the title paper under discussion provide the cross sectional optical micrographs of amorphous rods, taken at 10 mm from the bottom of the cast rod, for ø20 mm and ø30 mm rods, respectively. It is not clear why Fig. 4(b) is a kind of patch-work photograph, consisting of four sections. Straight boundaries or folds can be clearly seen both horizontally and vertically.

(6) Figure 5 shows a very homogeneous and smooth HREM photograph observed by the JEM-4000FX machine. Unfortunately, JEM-4000FX machine has not existed since 1990 in the Institute of Materials Research, Tohoku University, but JEM-4000EX machine was in use. Authors should be careful for their documentation.

(7) The HREM photograph, Fig. 5, is not understandable since the picture seems too smooth relative the other HREM photographs of glassy alloys previously published by the same authors,1) Matsuura et al.,2) and Hirata et al.3) When enlarging a part of Fig. 5, coarse pixels are easily detected in the amorphous matrix and the main panel picture of Fig. 5, shows rather coarse “pixels” relative to the photograph of Fig. 4. The coarse pixels could be the indicative of a computer-processed image. For this reason, the authors are requested to give information such as original pixel size, thickness of the sample, etc. for preparing the HREM image of Fig. 5.

(8) Since production of Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ glassy alloy rod with diameter of 30 mm using the suction casting method with copper mold4) was already reported by Inoue and Zhang in 1996,5) it is surprising that no reference was given to the earlier publication in the title paper. The second summarizing comment in the title paper “We produced a Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ glassy alloy rod of 30 mm in diameter by the cap-cast technique though the critical size of Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ glassy alloy rod was 20 mm by the conventional cast technique” is also misleading, since Inoue and Zhang claimed successful production of perfect metallic glass rod of 30 mm in diameter and 50 mm in length by means of the suction casting method in 1996.5) A comparative discussion of the two methods would have been useful to the readers.

The apparent internal contradictions, absence of essential information regarding the arc-melting equipment and lack of sufficient evidence to support the claim of amorphous state, make it difficult for readers to comprehend and appreciate fully the contents of the title paper.

REFERENCES