Publication IV

E. Soinila, T. Pihlajamäki, S. Bossuyt, H. Hänninen. A combined arc-melting and tilt-casting furnace for the manufacture of high-purity bulk metallic glass materials. *Review of Scientific Instruments*, 82, 1–4, doi:10.1063/1.3606444, 2011.

REVIEW OF SCIENTIFIC INSTRUMENTS **82**, 073901 (2011)

A combined arc-melting and tilt-casting furnace for the manufacture of high-purity bulk metallic glass materials

E. Soinila,[a)] T. Pihlajamäki, S. Bossuyt, and H. Hänninen
Department of Engineering Design and Production, Aalto University School of Science and Technology, Espoo, Finland

(Received 12 January 2011; accepted 9 June 2011; published online 8 July 2011)

An arc-melting furnace which includes a tilt-casting facility was designed and built, for the purpose of producing bulk metallic glass specimens. Tilt-casting was chosen because reportedly, in combination with high-purity processing, it produces the best fatigue endurance in Zr-based bulk metallic glasses. Incorporating the alloying and casting facilities in a single piece of equipment reduces the amount of laboratory space and capital investment needed. Eliminating the sample transfer step from the production process also saves time and reduces sample contamination. This is important because the glass forming ability in many alloy systems, such as Zr-based glass-forming alloys, deteriorates rapidly with increasing oxygen content of the specimen. The challenge was to create a versatile instrument, in which high purity conditions can be maintained throughout the process, even when melting alloys with high affinity for oxygen. Therefore, the design provides a high-vacuum chamber to be filled with a low-oxygen inert atmosphere, and takes special care to keep the system hermetically sealed throughout the process. In particular, movements of the arc-melting electrode and sample manipulator arm are accommodated by deformable metal bellows, rather than sliding O-ring seals, and the whole furnace is tilted for tilt-casting. This performance of the furnace is demonstrated by alloying and casting $Zr_{55}Cu_{30}Al_{10}Ni_5$ directly into rods up to ø 10 mm which are verified to be amorphous by x-ray diffraction and differential scanning calorimetry, and to exhibit locally ductile fracture at liquid nitrogen temperature. [doi:10.1063/1.3606444]

I. INTRODUCTION

Bulk metallic glasses (BMG) are amorphous metals, with a diameter larger than 1 mm, that solidified without detectable crystallization. Upon heating from the solid state these alloys exhibit a glass transition, after which they remain metastable for a finite length of time in the super-cooled liquid region, before crystallizing. Enhanced stability against crystallization is usually achieved by alloying multiple elements with significant difference (>12%) in atomic radius and negative heats of mixing among constituent elements. The critical casting diameters of known BMG alloys typically range from 1 mm to 100 mm. BMG alloys have been found in many different alloy groups (Pd-, Mg-, Ln-, Zr-, Ti-, Fe-, Co-, Ni-, and Cu-based systems) and new alloys have been discovered and reported with a variety of different properties. By casting BMG alloys, without cold working or heat treatment, complex shapes can be produced with excellent mechanical properties: purely elastic deformation up to a yield strain of typically 2%, resulting in tensile strength from 1500 MPa to 5500 MPa, with Young's modulus from 70 GPa to 275 GPa. The lack of grain boundaries in the BMG materials also results in very accurate surface finish and enhances corrosion resistance. Several recent reviews testify to the widespread interest in these materials both from a fundamental science perspective and for practical applications.[1–3]

Different methods may be used to produce amorphous metals, each with its own advantages and disadvantages, whose relative importance depends on the alloy composition and the intended purpose. Strictly speaking, an amorphous solid is called a glass only if it was formed when a liquid state underwent a glass transition. Thus, metallic glasses are formed by melting the constituents to obtain a molten alloy with the desired composition, and then quenching the molten alloy below its glass transition temperature. Often, pre-alloying to obtain the desired composition and quenching to the glassy state are entirely separate processes, carried out in different apparatuses. Prior to the discovery of bulk glass-forming alloy compositions, the rapid quenching methods required to avoid crystallization for most metallic glass-formers meant that these materials could be produced in glassy form only as thin ribbons, foils, or wires. The significance of BMGs can be attributed in large part to the versatility of metal mold casting methods in producing different shapes, not merely larger objects, out of metallic glass. If needed, casting can be followed by additional shaping or patterning steps—involving machining operations or superplastic forming in the viscous supercooled liquid region[4]— but usually the pre-alloying and casting steps are decisive for the quality of the final part.

For alloying, induction melting and arc-melting under inert atmosphere are commonly used, both with water-cooled copper crucibles. Both methods allow precise control of the melting process in laboratory scale production. Typically, the process chamber is repeatedly evacuated to a pressure around 0.1 Pa or lower and backfilled with purified argon, then purged of any remaining oxygen by titanium gettering before the constituent metals are melted for alloying. It is standard practice to flip over the pre-alloyed ingot and remelt it, several times,

---

[a)] Electronic mail: Erno.Soinila@hut.fi.

to ensure that its composition is uniform. When the process chamber must be opened to air to flip the ingot, renewing the inert atmosphere takes time, wastes argon, and risks contaminating the BMG with oxygen. Oxygen is harmful for BMG manufacture because, for some of the phases whose crystallization competes with glass formation, the crystallization kinetics are enhanced by oxygen.[5] As a result, BMG samples contaminated with oxygen typically are inferior to high-purity samples.[6–8] So not only is it quicker and more economical to perform the necessary manipulations of the ingot without repeatedly opening the process chamber; it also produces better samples.

For casting BMG, variants of metal mold casting are most commonly used. The method of quenching described in the earliest reports of bulk metallic glass formation in the Pd-Ni-P system[9,10] —and earlier work on marginally bulk glass forming Pd-Si based alloys[11]— did not involve metal mold casting. For some alloys, direct quenching of remelted pre-alloyed ingots in a fused silica container, especially in combination with fluxing, is still the preferred method for making high-quality BMG samples. However, it is difficult to produce complex shapes by this method, and the dimensional tolerances and surface quality obtained by direct quenching methods are not as good as those obtained by metal mold casting. A relatively simple version of metal mold casting consists of induction melting a pre-alloyed ingot in a fused silica crucible that has an orifice at the bottom, and then applying gas pressure to eject the molten BMG forming alloy into a mold placed beneath the crucible. High vacuum induction melting and argon pressure casting apparatus, with a linear feedthrough for moving the fused quartz crucible from the induction coil to the mold orifice, was found to be very versatile in easily producing different specimen shapes, such as rectangular and cylindrical rods,[12,13] wedges,[14] tubes,[15] and "dogbone" tensile specimens.[16] In a laboratory setting—where process conditions are often varied—it is particularly convenient to be able to view the sample through the quartz crucible during melting. However, because the same quartz crucible is a possible source of oxygen contamination,[7] it may sometimes be preferable to use other crucible materials, such as graphite. More sophisticated casting methods such as suction casting, tilt casting, squeeze casting, and cap casting may produce better quality specimens, e.g., because they can more consistently and more uniformly fill the mold. In particular, BMG specimens produced by the combination of tilt casting with cap casting or squeeze casting, compared to those produced by conventional tilt casting, have been reported to exhibit larger critical casting diameter[17] and improved ductility.[18]

II. DESIGN METHODOLOGY

It is a truism of high vacuum technology that each feedthrough and each seal represents a leak. Sliding O-ring seals, where a moving surface slides against the O-ring that provides the vacuum seal, are particularly prone to leaking. Also, when a vacuum chamber has been opened to atmosphere, it takes a long time to evacuate moisture adsorbed from the air onto the inside surfaces of the vacuum chamber.[19–21] To provide the high-purity conditions desired for BMG processing, the main process chamber should therefore have as few feedthroughs and as little surface area as possible. Nevertheless, the apparatus should allow the full range of motions and manipulations needed to carry out each step of the process, preferably without opening the chamber to atmosphere.

Based on previous experience[22,23] with both induction- and arc-melting for alloying and with various methods for casting, a choice was made to construct a multifunctional arc-melting and tilt-casting apparatus.

It is equipped with a manipulator arm so that, for pre-alloying, the sample can be flipped and remelted without opening the chamber. It also has provisions for piston suction casting and cap casting for small specimens. For a wide range of alloy compositions and sample sizes, the complete process from pre-alloying to high-quality net-shape casting can be carried out in a continuous sequence using this apparatus. Furthermore, the critical feedthroughs in this apparatus feature ultra-high vacuum construction methods, using flexible metal bellows for all moveable parts, and an all-metal gas line connects the chamber to a supply of high-purity inert gas. Thus, a high-purity atmosphere can be maintained throughout the entire processing sequence.

Tilt-casting under high purity conditions is seen as a method to reduce the incidence of casting defects, and produce samples of the highest quality.[24] The reasoning is that impurities in a casting process are collected on the surface of the melt, so that the cleanest alloy with the least inclusions is found in the interior of the melt. Also, material from cold spots at the bottom of the sample, where it touches the hearth during melting, may not be completely molten or sufficiently overheated. Tilt-casting is a comparatively gentle casting method, where the molten metal moves as one large drop of liquid instead of a narrow stream or atomized spray. The flow pattern is such that the melt charge is smoothly turned inside out into the mould and the material from the bottom and from the surface of the melt, if it is not part of the excess material left in the nozzle when the mould is completely filled, is mostly the last material to flow through the mould orifice. Thus, tilt-casting fills the mould primarily with the cleanest part of the melt. By contrast, when the mould is filled by squirting the melt out of a crucible through an orifice, the turbulent melt flow involves the rapid creation of new surface, which is sealed together again as the mould is filled. Even in high purity conditions, this process distributes the impurities from the melt surface to the interior of the specimen, resulting in inclusions. It may also cause significant variations in thermal history between adjoining material, affecting crystallization behavior, and residual stresses. Small amounts of inclusions and localized residual stresses may be unimportant for some measures of a specimen's quality, but eliminating them can significantly improve properties related to fracture and fatigue,[8] for instance. Tilt-casting effectively minimizes both the amount of newly created melt surface and complexity of the fluid flow pattern during the casting process. As a result, compared with casting methods where the mould is filled by turbulent flow, it produces specimens with a more uniform and consistent thermal history, fewer inclusions, and essentially no porosity.

III. DESIGN DESCRIPTION

The main chamber was constructed by modifying a standard 250 mm ISO-K T-section, oriented so that the flanges are at the top, bottom, and back of the chamber, as shown in Fig. 1. The arc-melting electrode passes through the top flange, the water-cooled hearth is raised from the bottom flange, and vacuum pumping is done through the back flange. In a similar setup to that reported by Arajs,[25] three additional flanges were TIG-welded to the chamber, providing feedthroughs for lighting, ingot manipulation, and viewing. Connections for suction casting and cap casting, and extra room for the moulds, are provided in an extension to the back flange. The water-cooled copper hearth inside the chamber features a single large melting trough with a pouring nozzle leading to the mould orifice, and a smaller trough for titanium gettering. The hearth is attached from below, to avoid any "internal leaks" from gas pockets that might otherwise be trapped between the hearth and the chamber. A standard ISO-K 200 O-ring seal with centering ring separates the vacuum from the cooling water circulating underneath the copper hearth. Belleville spring washers ensure that differential thermal expansion when the furnace is operated does not cause excessive decreases or increases in the clamp force maintained on the O-ring seal. Heli-Coil$^{\mathrm{TM}}$inserts help prevent damage to the threaded bolt holes in the copper hearth, considering that these must support bolt tension up to 1 kN with thermal cycling. To load a new charge into the furnace, the assembly of the bottom flange with the copper hearth is released from the rest of the chamber and lowered on a pneumatic lift provided for that purpose.

An arc-melter necessarily includes a feedthrough for the arc-melting electrode: a water-cooled conductor that can carry an electrical current up to 500 A and can handle the 30 kV high-voltage arc-ignition spark. This current needs to be electrically isolated from the chamber potential at operating pressures and atmospheres to avoid damage to the chamber. Furthermore, the electrode should be moveable; with a freely moveable electrode tip, the operator can deliver the energy of the plasma arc precisely where it is needed to melt the sample. The feedthrough should allow a range of motions covering every possible position of the sample in the melting trough as well as the titanium getter. This freedom of movement is realized with a flexible edge-welded metal bellows, between the top flange of the chamber and the electrical feedthrough for the electrode. The electrical feedthrough is constructed of two fluoropolymer insulators clamped onto either side of a copper flange which is brazed onto the electrode rod. Standard ISO-K 100 O-ring seals and centering rings seal the vacuum side. The tungsten electrode tip is secured with two screws to the brazed electrode tip assembly (visible at the top of Fig. 2) which seals the end of the water-cooled electrode rod.[25]

To assist the operator with delicate movements of the electrode tip and to prevent movements that would damage the hearth or the bellows, a mechanism for supporting the electrode is also necessary. The weight of the electrode rod and the atmospheric pressure when the chamber is evacuated amount to a force in excess of 800 N drawing the electrode towards the copper hearth. A mechanism with pneumatically actuated servo control in the vertical direction carries this load. At the touch of a valve on the electrode handlebar, near the right-hand thumb of the operator, precise adjustments can be made to the elevation of the electrode tip above the hearth. The attachment of the electrode rod to this mechanism by a pair of concentric gimbals lets the operator tilt the electrode rod to move the electrode tip forwards, backwards or sideways. Similarly, a clamp, connected by a ball joint to another pneumatically actuated servo mechanism, supports the sample manipulator arm.

Tilt-casting requires a mechanism for pouring the melt from the crucible into the mold. Often this is done with a sliding O-ring seal, in which a rigid connector carrying cooling water for the metal crucible also allows to tilt the crucible towards the mold. In this apparatus, the whole chamber is tilted. This eliminates a potentially troublesome sliding O-ring seal, but requires a more elaborate structure to support the chamber.

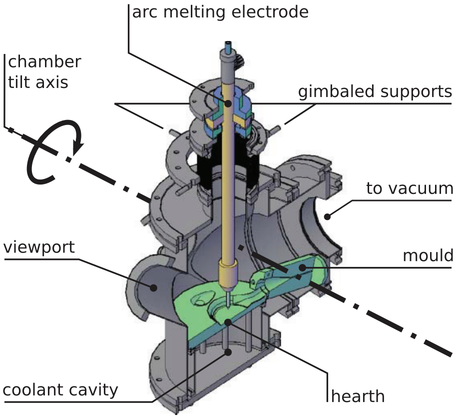

FIG. 1. (Color online) Cutout view showing the design of the vacuum chamber.

FIG. 2. (Color online) The arc-melting of a BMG alloy ingot on top of the water-cooled copper hearth. On the right is the tip of the manipulator used to flip the ingot upside-down between melting runs. The mould orifice and the melt pouring nozzle leading to it can be seen behind the electrode tip assembly.

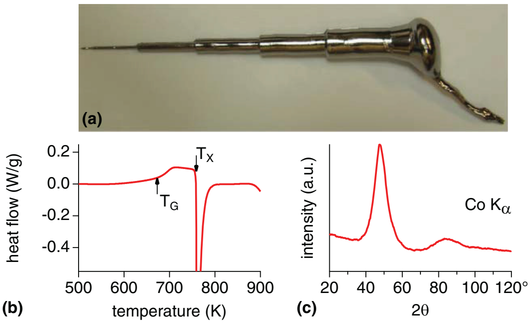

FIG. 3. (Color online) (a) Tilt- and suction-cast specimen with 1, 3, 5, 7, and 10 mm diameters. (b) Typical glassy DSC measurement from the tilt- and suction-cast BMG-rod showing distinctive glassy region between T_G and T_X. (c) X-ray diffraction (Co K_α) pattern of a tilt- and suction-cast specimen shows amorphous structure for ø 10 mm. Samples were prepared with a water-cooled aluminium oxide impregnated cutoff wheel. Cutoff wheel residue was removed by polishing with 1 μm diamond paste when necessary.

IV. RESULTS AND DISCUSSION

The results obtained with the constructed furnace are more focused on evaluating the functionalities of the furnace than the properties of the particular cast specimens. Several samples of Inoue alloy $Zr_{55}Cu_{30}Al_{10}Ni_5$ (At. %) was tilt- and suction-cast into a mold with 10, 7, 5, 3, and 1 mm diameters, as shown in Fig. 3(a). The x-ray diffraction spectrum from the largest cast diameter is shown in Fig. 3(c). In each case, a broad diffuse peak typical of the amorphous alloy was seen, confirming that the as-cast samples did indeed vitrify during the casting process. A differential scanning calorimetry (DSC) study shown in Fig. 3(b) was performed to verify the glassy nature of the cast alloy. The measured glass transition onset and crystallization onset temperatures were $T_G = 673.1$ K and $T_X = 758.9$ K, respectively, with a 40.8 J/g heat release in the primary crystallization peak.

Complete characterization of the purity of the argon gas under actual process conditions and the purity of the resulting specimen would be interesting, but would require much additional time and specialized instrumentation. However, the work of Keryvin *et al.*[8] allows to use low-temperature toughness as a proxy for sample purity. Studying the effect of sample purity on fracture behavior for the same $Zr_{55}Cu_{30}Al_{10}Ni_5$ alloy, they observed that at liquid nitrogen temperature, only the highest-purity samples still exhibited fracture surfaces with the vein-like features typical of locally ductile failure in metallic glasses. Therefore, beams of approximately 1 mm × 1 mm × 10 mm were cut from the ø 10 mm and ø 7 mm parts of a specimen, cooled in liquid nitrogen, placed over a gap in a bench vise and broken using a hammer and chisel. Figure 4 shows a fracture surface typical of these experiments with specimens produced in the constructed furnace, indicating that these specimens are similar to the highest-purity specimens of this alloy.

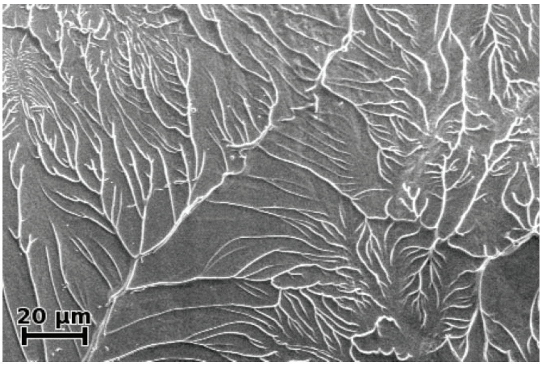

FIG. 4. Fracture surface of a small beam cut from the specimen shown in Fig. 3(a), broken at liquid nitrogen temperature in a 3-point bending geometry.

V. CONCLUSIONS

A combined tilt-casting arc-melting furnace was designed and constructed for the preparation of high-quality bulk metallic glass specimens. Using this apparatus, the complete process from pre-alloying to final casting can be carried out in one sequence, without need to vent and re-estabilish the inert atmosphere. Specimens of $Zr_{55}Cu_{30}Al_{10}Ni_5$ cast into cylinders up to 10 mm diameter using this apparatus were confirmed to be glassy and to exhibit fracture behavior similar to the highest-purity specimens of this alloy studied elsewhere.

ACKNOWLEDGMENTS

Funding by TEKES and the Academy of Finland are greatly appreciated for making this work possible. The staff of Department of Engineering Design and Production and Lydwin Rös from Trinos Vacuum are acknowledged for help with the numerous manufacturing steps. The discussions with Assistant Professor Yoshiko Yokoyama, Jarmo Raiskio, Markku Heino, Heikki Vestman, Jari Hellgren, Laura Tiainen, Samuli Laine, Paula Kainu, Voitto Vanhatalo, Kaj Pischow, and the Savcor Research and Development team are appreciated.

[1] A. Inoue and N. Nishiyama, MRS Bull. **32**, 651 (2007).
[2] M. Chen, Annu. Rev. Mater. Sci. **38**, 445 (2008).
[3] C. Schuh, T. Hufnagel, and U. Ramamurty, Acta Mater. **55**, 4067 (2007).
[4] J. Schroers, Adv. Mater. **22**, 1566 (2010).
[5] X.-H. Lin, W. L. Johnson, and W.-K. Rhim, Mater. Trans., JIM **38**, 473 (1997).
[6] R. D. Conner, R. E. Maire, and W. L. Johnson, Mater. Sci. Eng., A **419**, 148 (2006).
[7] I. Seki, D. Louzguine-Luzgin, and A. Inoue, Mater. Trans. **48**, 821 (2007).
[8] V. Keryvin, C. Bernard, J. Sangleboeuf, Y. Yokoyama, and T. Rouxel, J. Non-Cryst. Solids **352**, 2863 (2006).
[9] A. Drehman, A. L. Greer, and D. Turnbull, Appl. Phys. Lett. **41**, 716 (1982).
[10] H. Kui, A. L. Greer, and D. Turnbull, Appl. Phys. Lett. **45**, 616 (1984).
[11] H. Chen and D. Turnbull, Acta Metall. **17**, 1021 (1969).
[12] A. Inoue, T. Zhang, and T. Masumoto, Mater. Trans., JIM **31**, 425 (1990).
[13] A. Peker and W. L. Johnson, Appl. Phys. Lett. **63**, 2342 (1993).
[14] A. Inoue, Y. Shinohara, Y. Yokoyama, and T. Masumoto, Mater. Trans., JIM **36**, 1276 (1995).
[15] A. Inoue, T. Saito, H. Yamamoto, and T. Masumoto, J. Mater. Sci. Lett. **12**, 946 (1993).

[16] R. D. Conner, H. Choi-Yim, and W. L. Johnson, J. Mater. Res. **14**, 3292 (1999).

[17] Y. Yokoyama, E. Mund, A. Inoue, and L. Schultz, Mater. Trans. **48**, 3190 (2007).

[18] Y. Yokoyama, K. Fukaura, and A. Inoue, Intermetallics **10**, 1113 (2002).

[19] J. Hanlon, *A User's Guide to Vacuum Technology*, 1st ed. (Wiley, New York, 1988).

[20] H. Hablanian, *High Vacuum Technology, A Practical Guide*, 1st ed. (Marcel Dekker, New York, 1990).

[21] N. C. Harris, *Modern Vacuum Practice*, 1st ed. (McGraw-Hill, London, 1989).

[22] E. Soinila, M.S. thesis, Helsinki University of Technology, 2005.

[23] E. Soinila, Lic.S. thesis, Helsinki University of Technology, 2009.

[24] Y. Yokoyama, private communication (2008)

[25] S. Arajs and G. Wray, J. Phys. E: Sci. Instrum. **2**, 518 (1969).