Electron Beam Welding of Zr$_{50}$Cu$_{30}$Ni$_{10}$Al$_{10}$ Bulk Glassy Alloys

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By using a conventional electron beam welding machine, an electron beam welding of Zr$_{50}$Cu$_{30}$Ni$_{10}$Al$_{10}$ bulk glassy plates has been achieved in the welding condition leading to the suppression of heat affected zone (HAZ). In order to obtain the cooling rate, which is sufficient for glass formation, the welding speed was controlled to be higher than 100 mm/s and the beam-radiated area should be limited to be smaller than 0.8 mm in diameter. Joint strength of the welded bulk glassy plate is about 1400 MPa, which is lower by 15% than the tensile strength (1650 MPa) of the glassy alloy. The fracture of the welded alloy plate occurs along shear slip plane across the welded area, reflecting good ductility in the welded area of the Zr$_{50}$Cu$_{30}$Ni$_{10}$Al$_{10}$ bulk glassy alloy.

(Received May 30, 2002; Accepted August 2, 2002)

Keywords: electron beam welding, Zr$_{50}$Cu$_{30}$Ni$_{10}$Al$_{10}$ bulk glassy alloy, heat affected zone, crystallization, joint strength

1. Introduction

Recent development of bulk glassy alloys$^1$ has lead to a break through in basic science and engineering of metallic materials. However, there have been some problems for further extension in practical use of bulk glassy alloys. As one of the problems, one can list up a welding (joining) technology, because the bulk glassy alloys have been expected to be used as structural materials in various fields. It is well known that most of amorphous alloys are embrittled by heat affection leading to structural relaxation, phase separation and crystallization. More recently, several results on welding/joining have been reported for Zr–Al–Ni bulk glassy alloy and steels.$^2,3$ The welding between the Zr-based bulk glassy alloy and Zr metal has been reported$^4$ by using the Zr$_{41}$Ti$_{14}$Cu$_{12}$Ni$_{10}$Be$_{23}$ bulk glassy alloy with a critical cooling rate of about 2 K/s. This result indicates that the bulk glassy alloy with a critical cooling rate less than 2 K/s can be welded. We have tried to weld Zr$_{50}$Cu$_{30}$Ni$_{10}$Al$_{10}$ bulk glassy alloy with a critical cooling rate of about 12 K/s by the electron beam welding technique. The trial is very important because the Be-containing glass alloy is not always a safe material for human body and environment atmosphere. However, the use of the latter Zr-based alloy requires improvement of the welding technique for the formation of welded structure without crystalline phases. It has previously been reported$^5$ that Zr–Cu–Al–Ni glassy alloys are formed by the continuous casting method. The cast structures of continuously solidified bulk glassy alloys were analyzed on the basis of the cast structure diagram$^6$ with G versus V axes, where the G and V mean the temperature gravity at solid and liquid (S/L) interface and velocity of S/L interface, respectively. The difference between the continuous casting and electron (e-) beam welding of bulk glassy alloys is attributed to the molten area of the sample. The cooling medium in the continuous casting process is He atmosphere and water jacket copper hearth, while that in the e-beam welding process results from the non-welded region of samples. In the e-beam welding, the cooling rate of the welded area in the sample depends on the sample shape, and the shape is fixed in a constant size of 20 mm × 40 mm × 2.5 mm in this study.

In this study, we tried to weld Zr$_{50}$Cu$_{30}$Ni$_{10}$Al$_{10}$ bulk glassy plates by the electron beam technique, in which the energy and shape are controlled to restrain the embrittlement of HAZ and melt regions. In order to find an optimum welding condition of the bulk glassy alloy, we examined the structure and strength of the e-beam welded area obtained in various e-beam welding conditions.

2. Experimental Procedure

In order to obtain a sufficient cooling rate in the e-beam welded area, the beam radius and profile were examined in several beam current conditions. The e-beam welding is characterized$^9$ to make a beam hole in the center of beam-radiated area, and the preparation of the beam hole brings about a narrow welded area and homogeneous bonding structure. In actual, the preliminary experiment of the e-beam welding of the bulk glassy alloy is necessary to clarify the relationship between the welded area and the cooling rate. In the preliminary experiment, we measured a beam profile and its control method. The e-beam welding of conventional materials has used a defocus e-beam to produce a wide bead mark on the butt joint. However, the e-beam for the bulk glassy alloy must be focused on the sample surface to prepare the stable beam hole with low beam energy. This is because the excess beam energy occurs heat-affected embrittlement due to crystallization or structural relaxation in the melt and HAZ. The beam profiles were measured by using the Faraday coupling methods$^8,10$ and the shapes were also controlled by changing condenser lens current in the several beam current conditions. The beam profile should be a sharp and symmetrical one to restrain a molten area and achieve homogeneity. Furthermore, the beam profile of the shoulder point (edge of the beam) should be drastically increased to restrain the excess heat affect on the non-welded region of the bulk glassy alloy.
A quaternary Zr$_{50}$Cu$_{30}$Ni$_{10}$Al$_{10}$ alloy ingot was prepared by arc melting pure Zr, Cu, Al and Ni metals in an argon atmosphere. The alloy ingot was completely remelted, and squeeze cast into a plate shape with a width of 50 mm, a length of 60 mm and a thickness of 3 mm by a squeeze casting method. The bulk glassy plates were welded with an e-beam welding machine of Mitsubishi Electronic Co. Ltd. (30kW class) under an evacuated atmosphere of about 1 Pa. The e-beam welding conditions were as follows;
(1) accelerate voltage: 70 kV,
(2) stage moving velocity (welding speed): 16.7 to 250 mm/s,
(3) beam current: 5 to 120 mA, and
(4) $a_b$ value: 1 as just on focus.
Where the $a_b$ value is the ratio of focus distance to specimen surface distance from electron lens. The e-beam welded structure was examined by optical microscopy (OM) and scanning electron microscopy (SEM), and the compositions of several phases in the samples were determined with an electron probe microanalyzer (EPMA). Tensile strength of the e-beam welded sample was examined at an initial strain rate of $6.7 \times 10^{-3}$ s$^{-1}$ by using an Instron tensile testing machine equipped with a wire resistance strain gage meter. Hardness was measured by a micro Vickers hardness tester under a load of 2.9 N for a loading time of 15 s.

3. Results and Discussion

The development of bulk glassy alloys with a low critical cooling rate is expected to bring about the break through of size restriction. It also leads to the possibility of welding. The most important point in the welding of bulk glassy alloys is the reformation of glassy phase in the welded molten region through the suppression of crystallization in the HAZ region. In order to suppress the crystallization in the HAZ, the melted region must be reduced. The radiated area by electron beam should be smaller than the circle with 1 mm in diameter. In this study, the diameter of the electron beam was about 0.8 mm at the just focus condition of electron lens. Furthermore, the electron beam welding method can have the narrower and deeper welded region. This peculiarity causes the formation of an electron beam hole, which is formed between the electron beam and molten alloy as shown in Fig. 1.

![Schematic illustration of e-beam welding mechanisms for the ordinary method (a) and for the present study (b).](image)

In order to evaluate the crystallization in the e-beam welded area for the bulk glassy alloy, a simplified heat flow calculation was performed. Rosenthal calculated the cooling rate in the bonding area by eq. (1),
$$ R = -k(T - T_0)^n. $$
Here $T$ is temperature of each point, and $T_0$ is the initial temperature as 300 K. $t$ is the time and $k$ and $n$ are coefficients.

The factor $k$ is also defined as follows,
$$ \begin{cases} k = 2\pi \kappa \rho C \left( \frac{V_w}{q} \right)^2 & (\text{thin}) \\ n = 3 \end{cases} $$
$$ \begin{cases} k = 2\pi \kappa \frac{V_w}{q} & (\text{thick}) \\ n = 2 \end{cases} $$
where $\pi$ is the ratio of the circumference of a circle to its diameter, $\kappa$ is thermal conductivity as $7.23 \times 10^{-3} \times T$ (J/s·m·K), $V_w$ (m/s) is speed of welding, $q$ is heat input, $C$
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...is specific heat as 10 (J/mol·K), ρ is density 6850 (kg/m³), and s is thickness of sample. The value of q is calculated by the product of acceleration voltage of 70 (kV) and beam current of Iₘ (mA) as q = 70 × Iₘ (w). The value of specific heat is underestimated, because the specific heat values of the liquid and supercooled liquid should be lower than that of the glassy solid. In this study, the shape of the bulk glassy alloy corresponds to the thin sample condition in eq. (2). Equation (1) representing the cooling rate can be modified as follows,

\[ R = 3.38 \times 10^{-5} \left( \frac{V_w}{I_b} \right)^2 T (T - T_0)^3. \] (4)

This equation means that the high cooling rate can be obtained by the high welding speed and small input heat. It is ordinary condition to avoid the heat affect. However, the heating and cooling rates in the bonding region tightly depend on the heat flow capacity of the sample. That is, the large welding speed and small input heat do not always bring about high cooling rate. Because the high welding speed causes the wide melt region along welding direction under the constant heat flow capacity condition of the sample. Consequently, the e-beam welding demands the balance between the welding speed and input heat to obtain the satisfactory welded structure. By using eq. (4), cooling rates were calculated as shown in Fig. 2, under the following different conditions,

(a) Iₘ = 10 mA, Vₘ = 16 mm/s
(b) Iₘ = 50 mA, Vₘ = 100 mm/s
(c) Iₘ = 70 mA, Vₘ = 200 mm/s
(d) Iₘ = 100 mA, Vₘ = 250 mm/s

These conditions were determined on the basis of the experimental data described later. This figure indicates the possibility of the e-beam welding for the Zr-Cu-Ni-Al bulk glassy alloy. The cooling curve in these CCT diagrams(1,4) means the solidification condition in the welded region. Where Tᵢ values (Tᵢ = 1100, 1300, 1500, 1700, and 1900 K) are the start temperatures (t = 0) of several cooling curves in the welded region. In the figure (c) the fastest cooling rate, which can avoid the nose of CCT diagram, has the highest possibility to obtain the satisfactory bonding structure. Besides, the ordinary e-beam welding condition (a) in Fig. 2 means the crystallization in the welded region. Consequently, the best condition between Iₘ and Vₘ was selected to evaluate the bonding structure. As shown in Fig. 1(b), the best welding condition brings about the similar bead shapes at the top and bottom sides, because of the e-beam bore through the sample to make a beam hole. To determine the Iₘ value at each Vₘ value, the shape of the bead is the most important factor to evaluate the stability of the molten region. Figure 3 shows bead images on the top and bottom sides at several welding conditions. This figure shows the optimum structure of welded region at several welding speeds. In order to create the narrow melted alloy region leading to satisfactory cooling rate, the stable beam hole formation is the most important factor, which can be estimated by the similarity of the bead width between top and bottom side. Consequently, the welding conditions of (a) Iₘ = 10 mA, Vₘ = 16 mm/s, (b) Iₘ = 50 mA, Vₘ = 100 mm/s, (c) Iₘ = 70 mA, Vₘ = 200 mm/s and (d) Iₘ = 100 mA, Vₘ = 250 mm/s, were determined from the shapes of beads in Fig. 3. The characteristic points of the bead shape leading to the achievement of the optimum welding condition are determined as the difference of bead width on the top and bottom side and the fractal of bead width along welding direction on bottom side.

Figure 4 shows outer appearance of the welded bulk glassy tensile specimen (a) and the relationship between the tensile strength and beam current at different welding speed conditions of 100 mm/s, 200 mm/s and 250 mm/s, respectively. The eq. (4) means that the cooling rate increases with an increase of welding speed. However, the increasing of cooling rate depends on the heat flow capacity of the welded sample, whereas eq. (1) is assumed the specimen size as infinitely large. The large welding speed demands an excess beam current to form the stable beam hole. The excess beam current brings about wide molten alloy region along welding direction, because of the limited heat capacity of the speci-
men. Consequently, the optimum e-beam welding conditions of welding speed and beam current can be determined by the size of specimen. In this study, the specimen size was 20 mm × 40 mm × 2.5 mm. Furthermore, the change in the strength with beam current has a maximum point at several welding speeds. The welded structures, their micro X-ray diffraction patterns at the melt, the HAZ and matrix regions at these maximum strength conditions are shown in Fig. 5. In the figure, the optimum structure of the welded region of the Zr_{50}Cu_{30}Ni_{10}Al_{10} bulk glassy alloy is obtained at the welding condition of $I_b = 70$ mA and $V_w = 200$ mm/s. The welding condition is also leading to the highest tensile strength as shown in Fig. 4. In the other welding conditions, the welded structure of the bulk glassy alloys contain crystalline particles with an equiaxed dendrite shape in the vicinity of the interface between the melt and HAZ. The crystalline particles were identified as τ₃-phase from the X-ray diffraction patterns shown in Figs. 5(b) and (f). These OM images show a side...
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Fig. 4 Outer appearance of e-beam welded tensile specimen (a) and the relationship between the tensile strength of the e-beam welded region and the beam current at different welding speeds of 100, 200 and 250 mm/s.

Fig. 5 SEM images and small area X-ray diffraction patterns taken from the melt, the HAZ and matrix regions obtained at e-beam welding conditions $I_b = 50$ mA, $V_w = 100$ mm/s (a) (b), $I_b = 70$ mA, $V_w = 200$ mm/s (c) (d) and $I_b = 100$ mA, $V_w = 250$ mm/s (e) (f).
view of the tensile fractured specimens. The fracture morphology in the Zr\textsubscript{50}Cu\textsubscript{30}Ni\textsubscript{10}Al\textsubscript{10} bulk glassy alloy welded at the condition of $I_b = 70$ mA and $V_w = 200$ mm/s is composed of one shear slipped surface along a maximum shear stress plane. Besides, the fractured surfaces in the other welding conditions are characterized by brittle flat fracture mode, in which the fracture occurs along the plane perpendicular to the tensile direction. Figure 6 shows fractured surface SEM images of the e-beam welded Zr\textsubscript{50}Cu\textsubscript{30}Ni\textsubscript{10}Al\textsubscript{10} bulk glassy alloys obtained by welding at the conditions of $I_b = 50$ mA, $V_w = 100$ mm/s (a)–(e), $I_b = 70$ mA, $V_w = 200$ mm/s (f)–(j) and $I_b = 100$ mA, $V_w = 250$ mm/s (k)–(o). In this figure, brittle fractured surfaces (a) and (k) show the flat plane perpendicular to the tensile direction. The brittle fractured surface shows the crystalline brittle fracture mode as shown in (b)–(e) and (f)–(j). The brittle fractured surfaces were formed along the crystallized region, which was located at the interface between the melt and HAZ. Besides, at the welding condition of $I_b = 70$ mA and $V_w = 200$ mm/s, the good ductility of the e-beam welded region can be understood by the fractured direction and fracture surface mode. In the fracture surface, fracture initiation is identified in the deposit region near small crystalline particles as shown in Fig. 6(g). We cannot conclude that the origin of crystalline particle is due to the heat effect by e-beam welding, because the specimens were prepared by the arc squeeze casting process, and have the possibility of containing crystalline inclusions in the cast sample.\textsuperscript{15) However, almost all the fracture surface was formed by the slip deformation mode that is indicated by the well-grown vein patterns on the fractured surface shown in Figs. 6(h)–(j). Consequently, the best welding condition of $I_b = 70$ mA and $V_w = 200$ mm/s is not always perfect to obtain a single
alloy was estimated as 12 K/s \(16\) from the cooling rate data for the welded Zr\(_{50}\)Cu\(_{30}\)Ni\(_{10}\)Al\(_{10}\) bulk glassy alloy. The mean value of tensile strength for the welded Zr\(_{50}\)Cu\(_{30}\)Ni\(_{10}\)Al\(_{10}\) bulk glassy alloy will be changed by the roughness of solid/liquid interface. The cast structure of the welded region and the bonding strength of the e-beam welded region obtained at different welding conditions were noted. Estimated critical cooling rate \(R_c\) line for glass formation was also shown in the diagram.

glassy phase in the welded region. The mean value of tensile strength for the welded Zr\(_{50}\)Cu\(_{30}\)Ni\(_{10}\)Al\(_{10}\) bulk glassy alloy obtained at the condition of \(I_0 = 70\) mA and \(V_w = 200\) mm/s is 1400 MPa, which is lower by 15\% than that (1650 MPa) of the no-welded Zr\(_{50}\)Cu\(_{30}\)Ni\(_{10}\)Al\(_{10}\) bulk glassy alloy.

The solidification in the welding treatment is similar to the unidirectional solidification of the moving liquid at the solid and liquid (S/L) interface. The cast structure of the unidirectional solidified Zr\(_{60}\)Cu\(_{15}\)Ni\(_{10}\)Al\(_{10}\)Pd\(_{5}\) bulk glassy alloy was reported in 1995.\(^7\) In this report, the critical cooling rate for the glassy phase formation at the unidirectional solidification S/L interface is about 40 K/s. However, in the case of a V-shape copper mold equipped with thermocouples, the critical cooling rate with about 104 K/s\(^{13}\) for the formation of the Zr\(_{60}\)Cu\(_{15}\)Ni\(_{10}\)Al\(_{10}\)Pd\(_{5}\) bulk glassy alloy. Besides, the critical cooling rate of the arc-melted Zr\(_{50}\)Cu\(_{30}\)Ni\(_{10}\)Al\(_{10}\) alloy was estimated as 12 K/s\(^{16}\) from the cooling rate data of arc-melted Zr–Cu–Al–Ni alloys measured by a radiational thermometer. That is, the critical cooling rate changes significantly from 12 to 104 K/s, whereas the alloy compositions remain almost unchanged. The difference in the critical cooling rates is probably due to the difference in the amount of quenched-in nuclei in the molten alloy. The influence of the quenched-in nuclei on the continuous cooling transformation (CCT) curve was reported for Pd\(_{60}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\) bulk glassy alloy.\(^7\) The quenched-in nuclei cause the transition of CCT curve to shorter time side. The sort of quenched-in nuclei was considered as impurity phosphorus oxide inclusions. However, in the case of unidirectional solidification, there is a possibility of quenched-in nuclei without any impurities in the molten alloy. At the rough S/L interface, as exemplified for dendritic growth, a lot of nuclei are supplied into the melt by cutting off the arm of dendrite. The roughness of the S/L interface can be estimated by the G and V values in the cast structure diagram as shown in Fig. 7. In Fig. 7, the G and V values at the critical cooling rates of 12, 40 and 104 K/s are estimated as \(\circ\) to \(\bigcirc\) points in this figure by assuming the V values as 1, 10 and 100 mm/s, respectively. Consequently, the critical cooling rate for glass formation can be changed by the solidification condition. The relationship between cooling rate \(R\) and nose at CCT curves shown in Fig. 2 is not appropriate to estimate the optimum welding condition. In Fig. 7, the cooling rates at the melting and nose temperatures are also shown at several welding conditions by using eq. (4). This figure also points out that the glass formation in the welded region becomes difficult with an increase in V to over 250 mm/s. The increase in G value is more effective to obtain a glassy structure in the welded region. As a result, to obtain a glassy structure in the welded region, appropriate cooling methods leading to an increase in the heat capacity and heat flow ability of the specimens should be used.

4. Summary

In order to achieve the joining of the Zr\(_{50}\)Cu\(_{30}\)Ni\(_{10}\)Al\(_{10}\) bulk glassy alloy, the e-beam welding was performed. The structure of the welded region and the bonding strength of the e-beam welded specimens were examined. The results obtained are summarized as follows.

1. The welding condition of \(I_0 = 70\) mA and \(V_w = 200\) mm/s brings about the highest bonding strength of 1650 MPa as well as the formation of the glassy phase in the welded region.

2. The estimation of the welded structure on the basis of the only CCT diagram was not suitable. In the case of unidirectional solidification as exemplified welding, one should be paid attention to that the critical cooling rate to form glassy phase will be changed by the roughness of solid/liquid interface.

REFERENCES