Twin-Roll Strip Casting of Iron-Based Amorphous Alloys

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In this study, three Fe-base amorphous alloys with quite different critical cooling rates were subjected to twin-roll strip casting to see the possibility of fabricating amorphous sheet by the same process. Continuous cooling transformation (CCT) diagrams of the alloys were calculated using the heterogeneous nucleation theory coupled with thermal data obtained during cooling to evaluate their critical cooling rates and glass forming abilities (GFAs). It shows that the GFAs calculated by CCT diagram are in agreement with the experimental results, while the well known empirical thermal parameters do not agree with the experimental results. Optimum twin-roll strip casting conditions have been determined based on the calculated critical cooling rates and the simulated thermal behavior of the sheet during twin-roll strip casting.

Keywords: twin-roll strip casting, iron-base amorphous alloy, nucleation kinetics

1. Introduction

Bulk amorphous alloys constitute a novel and exciting class of metallic materials with unique physical and mechanical properties for structural and functional applications.1–4 However, there are several obstacles to overcome for successful application of these alloys. One of them is that most of these alloys require fairly large amounts of expensive alloying elements to form amorphous structure in bulk form, making them one of the most expensive alloy systems. To overcome such problem, extensive efforts have been conducted on developing bulk amorphous alloys based on relatively low cost alloying elements, e.g., Fe-base alloy systems.5–10 R&D efforts on these Fe-base bulk amorphous alloys are mainly concentrated on developing the alloys with enhanced glass forming abilities (GFAs) and mechanical properties. It has been reported that some of these alloy systems can be made into rod with 5 mm in diameter by drop casting11 and 16 mm in diameter by injection casting.12 However, there have been only few studies on the fabrication processes of these alloys.

It has been recently demonstrated that some of bulk amorphous alloys, e.g., Zr- and Cu-base alloys, can be continuously fabricated in sheet form by twin-roll strip casting which can produce flat rolled products directly from melt in a single step.13–16 As compared to Zr- and Cu-base alloys, Fe-base alloys generally have high liquidus temperature (∼550 K and ∼380 K higher than those of Zr- and Cu-base alloys, respectively) and the difference between liquidus temperature and glass transition temperature (Tg) is large (∼700 K for Fe-base alloys vs. ∼360 K and ∼450 K for Zr-base and Cu-base alloys, respectively). It requires that a large degree of undercooling should be obtained during twin-toll strip casting of Fe-base alloys. Such characteristics of Fe-base alloys would make it difficult to be continuously fabricated into sheet with amorphous structure by twin-roll strip casting.

The present study is aimed at studying the feasibility of fabricating Fe-base amorphous alloy sheets by twin-roll strip casting. Three Fe-base amorphous forming alloys with different GFAs were subjected to twin-roll strip casting. GFAs of these alloys were estimated based on the values of empirical thermal parameters, the supercooled liquid region ΔTx (= Tx - Tg), reduced glass transition temperature Tg (= Tg/Tl), and γ parameter (= Tx/(Tg + Tl)). Cooling sequence during twin-roll strip casting and continuous cooling transformation (CCT) diagrams were simulated to determine the optimum processing conditions at which desirable solidification behavior could be achieved.

2. Experimental Procedure

Nominal compositions of the alloys used in the present study are Fe63B15Zr8Cu6Mo7Al1 (P0), Fe70B13.5Zr6.5Co7Si3 (P1) and Fe68.4B23.4Y4.6Nb4 (P2). Alloy ingots were supplied by the Liquidmetal™ Technologies in USA. To evaluate their GFAs, ribbon samples of about 100 μm in thickness and rod samples of 1–3 mm in diameter were prepared by melt spinning and injection casting, respectively.

The alloys were subjected to the twin-roll strip casting using the twin-roll strip caster at POSTECH. For the P0 alloy, it was induction melted at 1642 K under Ar atmosphere. After melting, the molten alloy was transferred into tundish and strip cast in air. The roll gap was 1 mm and the rotating speed of rolls was 3 rpm (1.9 m/min). Similar conditions were used for the P1 and P2 alloy, except the melting temperature (1663 K for P1 and 1555 K for P2). The amorphous nature of the strip cast sheets, melt spun ribbons and injection cast rods were analyzed by X-ray diffraction (XRD) and electron microscopy analysis.

GFAs of these alloys were calculated by constructing the CCT diagrams for crystallization based on the results of thermal analyses and simulation using the heterogeneous nucleation theory. Thermal analyses were carried out in a differential thermal analyzer (SDT Q600, TA Instruments) under flowing high-purity Ar atmosphere at two different cooling rates (5 K/min and 20 K/min). The detailed procedures for thermal analyses and simulation are described elsewhere.17 To gain information on the optimum twin-roll
nucleation theory has been developed, which successfully described the crystallization behavior of the Zr-base Vit-1 alloy\(^1\)\(^7\) and Mg-Cu-(Y,Gd) alloy\(^2\)\(^0\) during cooling. The same approach has been used in the present study to compare the crystallization kinetics of the present Fe-base alloys during cooling. The values of density (\(\rho\)) used for calculation are 7140, 7250, and 7210 kg/m\(^3\) for P0, P1, and P2 alloys, respectively. Heat of fusion (\(\Delta H_f\)) is 188000 J/g for all alloys. Since the values of interfacial energy (\(\sigma\)) and viscosity (\(\eta\)) for the present alloy systems are not available, they were obtained from the previous investigations on similar alloy systems. Considering the values of interfacial energies for possible crystalline phases,\(^\text{21}\) bcc Fe, Fe\(_2\)B, and Fe\(_3\)B, interfacial energy is assumed to be 0.2 J/m\(^2\) for all alloys. The viscosity was calculated using the values of \(D^*\) (8), \(T_0\) (654 K) and \(\eta_0\) (0.00004 Pas) given by the previous investigation.\(^\text{19}\) The nucleation temperatures (\(T_n\)) were measured at two different cooling rates of 5 K/min and 20 K/min. The differences in nucleation temperatures (\(\Delta T_n\)) at between two cooling rate for P0, P1 and P2 alloys are 5 K, 2 K and 4 K, respectively. The calculated values of \(S_V\) (surface area of the heterogeneous nucleation sites in a unit volume) and \(\theta\) (wetting angle) are \(2 \times 10^{-21}\) m\(^{-1}\) and 23.72\(^\circ\) for P0 alloy, \(4 \times 10^{-19}\) m\(^{-1}\) and 14.2\(^\circ\) for P1 alloy, and \(5 \times 10^{-19}\) m\(^{-1}\) and 16.8\(^\circ\) for P2 alloy. Using these values, nucleation temperatures at various cooling rates are calculated and the results are expressed as CCT diagrams shown in Fig. 2. Critical cooling rates, \(R_c\), for P0, P1 and P2 alloys are calculated to be 54 K/s, 7700 K/s and 2060 K/s, respectively.

3.2 Optimum conditions for twin-roll strip casting

Among the processing variables of twin-roll strip casting, rotating speed of rolls has the most significant effect on the microstructure and casting efficiency of twin-roll strip cast sheets.\(^\text{22}\) When the rotating speed of rolls is too slow, temperature of the sheet reaches \(T_r\) before the sheet passes the roll nip point. In this case, the actual fabrication of the sheet by twin-roll strip casting might not be possible since the thickness of the fully amorphous sheet could not be reduced at the roll nip point due to its very high strength. On the other hand, when the rotating speed of rolls is too fast, there would be no sufficient heat extraction so that the center of the sheet is still in liquid state. In such case, the sheet could not be cast continuously since the sheet does not have enough strength to maintain continuity.\(^\text{13,14}\) It is also quite possible for the sheet to be crystallized when the temperature of the mid-thickness area of the sheet is high. It is expected that crystallization would not occur when the temperature of the sheet is lower than the temperature at common tangential point (\(T_c\))

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3. Results

3.1 Crystallization kinetics of the alloys

Figure 1 shows the XRD results of the melt spun and/or injection cast alloys. 2 mm rod sample of P0 alloy shows a typical smooth halo pattern, indicating the formation of amorphous phase. In the cast of 3 mm rod P0 alloy sample, it shows several crystalline peaks which match with \(\alpha\)-Fe peaks. P1 alloy shows the amorphous halo pattern in melt-spun ribbon sample, but its halo pattern is not as smooth as that of P0 alloy. 1 mm rod sample of P1 alloy shows sharp crystalline peaks which include \(\alpha\)-Fe peaks and some unidentified phase peaks. P2 alloy can be amorphized up to 1 mm injection cast rod sample.

The results of thermal analyses are shown in Table 1. In our previous study, the approach based on heterogeneous
between critical cooling curve and CCT diagram since the crystallization kinetics at low temperature is sluggish. Therefore, optimum conditions for the successful fabrication of amorphous alloy sheets by twin-roll strip casting are such that the mid-thickness temperature of the sheets at the roll nip point must be lower than the \( T_c \) of CCT diagram and must be higher than \( T_g \) of the alloy.

To obtain the optimum rotating speed of the rolls for Fe-base amorphous alloys used in this study, thermal behavior of the sheet during twin-roll strip casting was simulated with FLUENT and correlated with the constructed CCT diagrams. The calculated \( T_c \) for P0, P1, and P2 alloys are 1260 K, 1224 K, and 1150 K, respectively. Using the \( T_g \) and \( T_c \) as the lower and higher bound, respectively, the ranges of critical rotating speeds of rolls when the roll gap is 1 mm are calculated to be 2.7–7.3 rpm (1.7–4.6 m/min) for P0 alloy, 2.5–6.2 rpm (1.6–3.9 m/min) for P1 alloy, and 3.1–6.3 rpm (1.9–3.9 m/min) for P2 alloy. At these conditions, the ranges of cooling rates are 732–956 K/s for P0 alloy, 725–938 K/s for P1 alloy, and 735–877 K/s for P2 alloy.

Figure 3 shows the XRD patterns of the alloys strip cast with the rotating speed of rolls at 3 rpm (1.9 m/min). In the case of P0 alloy, some sharp peaks superimposed on the main halo are observed, suggesting that the strip cast P0 alloy consists of amorphous matrix with some crystalline particles, which have been identified as \( \alpha \)-Fe phase. In the case of P1 and P2 alloys, however, the broad halo of amorphous structure is absent and only sharp crystalline peaks are observed, indicating that the strip cast P1 and P2 alloys are fully crystallized during twin-roll strip casting. Figure 4 shows the microstructures of the strip cast alloys. As expected from the XRD results, the strip cast P0 alloy contains amorphous structure with some dendritic crystalline phase, while the strip cast P1 and P2 alloys have only crystalline phases.

4. Discussion

Table 2 shows the thermal properties of the alloys, along
with the well known empirical thermal parameters which can estimate the GFAs of amorphous alloys, the supercooled liquid region $\Delta T_m$ and reduced glass transition temperature $T_g$ can be calculated from experimental results. The evaluation of thermal parameters suggests that all three alloys have good GFAs and they can be produced as amorphous sheet by twin-roll strip casting. Based on the values of these thermal parameters, it can also be said that P2 alloy has the highest GFA, followed by P0 alloy and P1 alloy.

However, experimental evaluation of GFAs shows much different results from the estimation based on the values of thermal parameters. As shown in Fig. 1, P1 alloy was amorphized only by melt spinning, and P0 and P2 alloys could be made into amorphous structure in just 2 mm and 1 mm injection cast rod samples, respectively. Also, P0 alloy shows a higher GFA than P2 alloy although P2 alloy was expected to have the highest GFA among three alloys. Therefore understanding the crystallization kinetics during cooling is necessary to correctly evaluate GFAs.

In this study, CCT diagram based on the heterogeneous nucleation theory was selected to assess GFAs more precisely. For the construction of CCT diagram, thermal analysis during cooling should be conducted to get the values of $\Delta T_m$, $T_g$, and $\gamma$. It has been shown in our previous study that our approach based on the heterogeneous nucleation theory gives good agreement between calculated and experimental results despite the uncertainties associated with the values of nucleation parameters such as interfacial energy and viscosity, since the self-adjusting effect of $S_V$ and $\theta$ on crystallization kinetics complements an error which can be caused by the limited thermophysical data. When the cooling rate is fast, the melt tend to be supercooled as liquid rather than solidified. Higher $\Delta T_m$ means that the alloy can be easily supercooled to lower temperature and have a wider range of supercooled region. Therefore $\Delta T_m$ has close relationship with GFA. The values of $\Delta T_m$ are 5 K, 2 K and 4 K for P0, P1, and P2 alloys, respectively, suggesting that P0 alloy has the highest GFA among them. This is in agreement with the values of $R_c$ calculated from CCT diagrams. The calculated values of $R_c$ for P0, P1 and P2 alloys are 54 K/s, 7700 K/s and 2060 K/s, respectively. Therefore based on the values of $\Delta T_m$ and $R_c$, it shows that P0 alloy has the highest GFA followed by P2 alloy and P1 alloy, which agrees with the experimental results of XRD analyses. As mentioned above, thermal parameters based on the data obtained heating show the results much different from the experimental results. It indicates that for the estimation of GFAs, the parameters based on the data obtained cooling is much more reliable than those based on the data obtained heating, and therefore the analyses of crystallization kinetics during cooling are critical for precise evaluation of the GFAs of alloys.

It has been shown that amorphous sheet can be produced only for P0 alloy among three alloys investigated. The calculated cooling rates at the rotating speed of 3 rpm are about 790 K/s and 770 K/s at the surface and center of the sheet, respectively. At such cooling rates (i.e., at rotating speed of 3 rpm for P0 alloy), the mid-thickness temperature (896 K) of the sheet is well above $T_m$ and is also lower than $T_c$ of the CCT diagrams at roll nip point. Therefore it is expected that P0 alloy can be fabricated into the amorphous structure by twin-roll strip casting. However, it shows that P0 alloy sheet contains a small amount of dendritic crystalline particles in amorphous matrix. In contrast to P0 alloy, P1 and P2 alloys would be fully crystallized during twin-roll strip casting since the cooling rates at the critical rotating speeds of rolls are much slower than the $R_c$ of both alloys. It has been shown that the optimum condition for twin-roll strip casting is dependent on two factors; the degree of undercooling (i.e., the difference between melting temperature and mid-thickness temperature of the sheet) and the cooling rate at roll nip point. Figure 5 shows the variation of the cooling rate and the degree of undercooling at roll nip point with the rotating speed of the rolls. It shows that with increasing the rotating speed of rolls, the cooling rate increases but the degree of undercooling decreases. Since the amorphous structure can form by twin-roll strip casting when the center of the sheet at roll nip point is undercooled below $T_c$ and the $R_c$ is slower than the cooling rate achievable in twin-roll strip casting.

### Table 2 Thermal properties and the values of thermal parameters.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_x$ (K)</th>
<th>$T_y$ (K)</th>
<th>$T_l$ (K)</th>
<th>$\Delta T_x$</th>
<th>$T_g$</th>
<th>$T_{x}(T_{y} + T_l)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>845.4</td>
<td>930.2</td>
<td>1542.5</td>
<td>75.8</td>
<td>0.55</td>
<td>0.36</td>
</tr>
<tr>
<td>P1</td>
<td>819.9</td>
<td>856.3</td>
<td>1563.2</td>
<td>36.4</td>
<td>0.53</td>
<td>0.36</td>
</tr>
<tr>
<td>P2</td>
<td>864.2</td>
<td>947.9</td>
<td>1455.2</td>
<td>83.7</td>
<td>0.59</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Fig. 5 Schematic diagram showing the variation of the cooling rate and the degree of undercooling at roll nip point with the rotating speed of the rolls.
casting, there exists a range of the rotating speed of rolls which can produce amorphous structure. At below or above such range, amorphous structure cannot be formed. For example, increasing the rotating speed of rolls above the range increases the cooling rate, but also results in a decrease in the degree of undercooling so that the temperature of sheet becomes higher than $T_c$. This is different from the melt spinning process which shows an increase in both the cooling rate and the degree of undercooling with increasing the rotating speed of rolls resulting from the concurrent decrease in thickness of ribbon with increasing the rotating speed of rolls.

5. Summary

To determine the optimum twin-roll strip casting conditions at which amorphous sheet could be fabricated, thermal behavior during twin-roll strip casting and CCT diagrams of the alloys were simulated. Critical cooling rates of the alloys were calculated from the simulated CCT diagrams. It shows that there is a range of the critical rotating speeds of rolls which give enough cooling rates and degree of undercooling to produce amorphous structure. Actual twin-roll strip casting at the simulated optimum condition shows that Fe-base amorphous forming alloy can successfully be strip cast forming amorphous structure, despite their higher liquidus temperatures and larger differences between liquidus and glass transition temperatures ($T_g$) than those of other easier glass-forming bulk amorphous alloys.

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