Using Kissinger analysis and temperature field simulation we analyze the crystallization of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ bulk metallic glass (BMG) during laser welding. We obtain the continuous heating transformation curve, the distribution of temperature field, and thermal cycle curves from which the thermal analysis is performed. We find that the material in the welding fusion zone is fully penetrated and the temperature in the base material zone is far below the crystallization temperature. Laser welding experiments are conducted to validate the Kissinger analysis and the simulation results. The welded joints are examined and the results are consistent with the simulation prediction. Therefore, the Kissinger analysis and temperature field simulation provide a convenient and reliable way to predict the crystallization of BMG during laser welding, which is beneficial to optimize the welding process and guide the laser welding of BMG.

1. Introduction

Bulk metallic glasses (BMGs), compared with traditional crystalline alloys, have excellent physical, mechanical, and chemical properties, such as superior strength, hardness, elastic deformation limit, wear resistance, and corrosion resistance at ambient temperature.[1] Moreover, they behave like Newtonian fluid in the supercooled liquid region (SCLR) enabling easy processing.[2] Thus, BMGs have received most attentions in engineering applications and scientific research fields recently, including sport equipment, transformer, armour-piercing bullet, etc.[3] However, problems of size limitation and lack of workability restrict the wide application of BMGs. Especially, the size limitation caused by the rapid cooling during manufacturing procedure limits the applications of large size structure severely. To date, lots of efforts have been devoted to increase the size of BMGs materials, including optimization of preparation technology and welding process.[4] Therein, laser welding technique has been widely used to join BMGs via its high energy density, high welding speed, and little deformation, etc. Kim et al.[5] connected Cu$_{54}$Ni$_{6}$Zr$_{22}$Ti$_{18}$ using Nd:YAG laser beam. Wang et al.[6] reported the laser spot welding of Zr-based BMG. BMGs belong to metastable material at room temperature. In the laser welding, the microstructure trends to change and leads crystallization due to the heat effect. Hence, it’s especially important to analyze the crystallization and select appropriate parameters. Some works have been paid to the crystallization kinetics and thermal stability discussion. Xia studied the long-term stability of Nd$_{60}$Al$_{20}$Co$_{20}$ BMG using Kissinger and Vogel-Fulcher-Tammann analyses.[7] Liu et al.[8] investigated the crystallization of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ by differential scanning calorimetry. On the other hand, Li et al.[9] used the finite element method (FEM) to calculate the thermal cycle curves of BMG welding joints. However, very few reports refer to the crystallization prediction and process optimization in laser welding in the last decade. Trial and error method is still the main way to decide the welding parameters, which is inconvenient and costly. Therefore, it is necessary to propose a simple and effective method for crystallization analysis and prediction on laser welding of BMGs.

In this study, we obtained the continuous heating transformation (CHT) curve and the thermal cycle curves by Kissinger fitting and temperature field simulation, and then combined...
them to analyze crystallization of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ BMG under different parameters during laser welding. The results reveal that the BMG plates crystallize under low welding speed or high welding power. The laser welding experiments were carried out for validation, and the welded joints were examined by Keyence microscope, scanning electron microscope, and transmission electron microscope, respectively. The experimental results are consistent with the simulation, indicating that the Kissinger analysis and simulation of temperature field can be used to predict crystallization and optimize welding process.

2. Simulation

For BMG materials, the time–temperature–transformation (TTT) diagram and the CHT curve describe the thermal stability under heat effect. Thermal cycle curves depict the continuous temperature change of material along with the time. During laser welding, in order to maintain the amorphous state of welded joints, thermal cycle curves cannot intersect with the TTT diagram and the CHT curve, or crystallization will happen in the welding fusion zone (WFZ) and the heat affected zone (HAZ) respectively. This can be used to predict the crystallization and decide the welding parameters.

2.1. Kissinger Fitting

Attentions have been paid to the CHT curve and the research of the long-term stability of BMGs using the corollary of Kissinger analysis. The glass transition and crystallization reaction of BMG materials can be evaluated by the Kissinger equation:

\[
\ln \frac{T^2}{\alpha} = - \frac{E}{R T} + C
\]

where \( T \) corresponding to \( T_g \) and \( T_x \), \( \alpha \), \( E \), and \( R \) standing for the heating rate, active energy, and Boltzmann constant, respectively. Here \( C \) is a constant.

According to the \( T_g, T_x \) of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ BMG, the plots of \( \ln(T^2/\alpha) \) versus \( 1/T \) are obtained, as shown in Figure 1a. It is found that the characteristic temperatures meet the Kissinger fitting very well, as described by:

\[
\ln \frac{T_g^2}{\alpha} = \frac{107729}{T_g} = -148.2 + \frac{896}{RT_g}
\]

\[
\ln \frac{T_x^2}{\alpha} = -26.6 + \frac{234}{RT_x}
\]

Table 1. Parameters used in laser welding of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ BMG.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Power [kW]</th>
<th>Speed [m/min]</th>
<th>Argon gas flow [L/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.8</td>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>3.8</td>
<td>22</td>
<td>33</td>
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<tr>
<td>3</td>
<td>3.8</td>
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<td>20</td>
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<td>5</td>
<td>4</td>
<td>22</td>
<td>33</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>24</td>
<td>33</td>
</tr>
</tbody>
</table>

Table 2. The main parameters of the simulation.

<table>
<thead>
<tr>
<th>Corresponding temperature [K]</th>
<th>Specific heat capacity [J mol$^{-1}$ K$^{-1}$]</th>
<th>Thermal conductivity [W m$^{-1}$ K$^{-1}$]</th>
<th>Density [g cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>26.5</td>
<td>5.2</td>
<td>6.82</td>
</tr>
<tr>
<td>450</td>
<td>27.8</td>
<td>9.8</td>
<td>6.82</td>
</tr>
<tr>
<td>550</td>
<td>22.6</td>
<td>12.3</td>
<td>6.82</td>
</tr>
<tr>
<td>610</td>
<td>26</td>
<td>14.4</td>
<td>6.82</td>
</tr>
<tr>
<td>680</td>
<td>50</td>
<td>19.2</td>
<td>6.83</td>
</tr>
<tr>
<td>750</td>
<td>40</td>
<td>15.1</td>
<td>6.83</td>
</tr>
</tbody>
</table>
We put $\alpha = (T - 293)/t$ into Equation (3) and thus construct the CHT curve. The $t$–$T$ plots from Kissinger fitting and isothermal experiments are shown in Figure 1b. Obviously, the $t$ and $T_x$ of experimental data correspond to the CHT curve well, indicating Kissinger fitting is suitable for the long stability analysis of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ BMG.

2.2. Simulation of Temperature Field

SYSWELD, the professional simulation software, is used to provide distribution of temperature field and calculate thermal cycle curves in this work. In the previous work,[4] the SYSWELD software was used to simulate the laser welding under 7 m min$^{-1}$. The
results show that the welding joint maintains the amorphous structure, which is consistent with the experimental result. Therefore, the simulation using SYSWELD is effective and reliable. Generally, the energy to melt the materials is proportional to the laser power and laser spot size, but inversely proportional to the welding speed. The spot size is a constant with the limitation of laser equipment, so we only consider the laser power and speed. The model sample of Zr_{55}Cu_{30}Al_{10}Ni_{5} BMG has the dimension of \(18 \times 3 \times 1.2\) mm\(^3\). Table 1 lists the parameters for laser welding simulation and experiment, where the maximum welding speed is up to 24 m min\(^{-1}\). In addition, the main parameters used in the simulation are shown in Table 2 according to the references.\(^{[11]}\)

Before the simulation analysis, the finite element model of BMG plates was constructed by the Visual Mesh and the heat sources were established by the SYSWELD software, as shown in Figure 2. The model consists of BMG plates, reference line (RL) and welding line (WL). To obtain accurate simulation results, the elements in the WFZ and HAZ are much smaller than those in other regions. Six heat sources were checked.

![Fig. 4. The thermal cycle curves of nodes taken from the HAZ and the CHT curve of Zr_{55}Cu_{30}Al_{10}Ni_{5} BMG. (a)–(f) corresponds to samples 1–6.](image-url)
under three-dimensional Gaussian mode according to the welding parameters listed in Table 1. As shown in the inset of Figure 2, the red area with nail pattern is the WFZ, the blue area belongs to base material zone, and the HAZ is between the WFZ and the base material zone.

Figure 3 depicts the contour of the simulation temperature field on the cross section and surface at \( t = 0.65 \) s. In these six welded joints, the maximum temperature in the WFZ is larger than 2000 °C and the minimum temperature reaches 1545 °C. They both exceed the \( T_m \) of Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) BMG, indicating that the plates are fully penetrated. The blue region corresponding to the base material zone displays the temperature far below the crystallization temperature (\( T_c = 489 \) °C), so the material in the base material zone remains in amorphous state. With the increase of welding speed, the temperature decreases apparently. This is beneficial to inhibit crystallization. On the other hand, larger welding power results in higher temperature, which is helpful to penetrate the BMG plate completely. Accordingly, we should select appropriate match of welding power and speed to obtain the joints with fully penetration and glassy phase. The temperature located at the welding start point is 700 °C. This is because the quasi-steady-state temperature field has not been established yet at the beginning of laser welding.

For every welding joint, there are six nodes selected in the HAZ to describe temperature changes and calculate the thermal cycle curves. The results are shown in Figure 4. It can be seen that low welding speed leads to short distance between the CHT curve and the thermal cycle curves. Therein, the thermal cycle curves intersect with the CHT curve in Figure 4a, d, and e, indicating that the samples 1, 4, and 5 are crystallized after laser welding. No intersection point exists in Figure 4b, c, and f, revealing that the samples 2, 3, and 6 still maintain glassy nature. Therefore, larger power or lower speed trends to cause crystallization in the welding process of BMG materials. Once the fully penetration is obtained, we should select high welding speed or low welding power. In comparison with previous work\,[4] it can be found that high speed welding still leads to crystallization of BMG during laser welding. Obviously, we have to select appropriate range of welding parameters to ensure that the welding joints are fully penetrated and maintain glassy nature simultaneously.

According to the discussion mentioned above, we can predict the crystallization in the WFZ likewise. The nodes in the center of these six welding beads are selected and then the thermal cycle curves are constructed, as shown in Figure 5. The TTT diagram of Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) BMG\,[12] intersects with the thermal cycle curves under the speed of 20 m min\(^{-1}\) but separates from the curves with larger speeds. Obviously, the samples 1 and 4 crystallize in the WFZ due to the heat effect, and the other samples retain amorphous state. The results demonstrate the crystallization not only occurs in the HAZ but also in the WFZ. By contrast, crystallization is most likely to occur in the HAZ.

![Fig. 5. The TTT diagram of Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) BMG and the thermal cycle curves.](image)

3. Welding Experiment

3.1. Experimental

To validate the Kissinger fitting and the temperature field simulation for laser welding of Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\), the welding experiments were carried out. As-received BMG plates are obtained from the BYD Co. Ltd. According to the dimension designed in simulation, we cut the BMG billets into small plates with the size of \(18 \times 3 \times 1.2\) mm\(^3\).
The laser welding experiments were conducted by Ytterbium fiber laser (YLR-4000) under continuous wave mode according to the parameters listed in Table 1, where the focal spot size is about 0.4 mm. The welding beads were protected using argon atmosphere for restraining the plasma and cooling the welded samples. Then we cut the welded samples into small blocks for metallographic sample preparation by CNC precision dicing/cutting machine (Shenyang Kejing Instrument Co., Ltd, EC-400), and polished them using 12" precision auto lapping/polishing machine (MTI, UNIPOL-1202) for evaluating the structural change and bonding quality of the joints.

3.2. Results and Discussion

The macro-planar views of six welded samples and the morphology of cross section were observed using Keyence microscope (VHX-1000), as shown in Figure 6. The welding beads are different because of different welding parameters. Generally, large welding power or low speed leads to wide welding seam or deep penetration. Meanwhile, the small inclined angle was formed by a typical nail head shape, which belongs to the HAZ. From the figures at the bottom, it can be seen that the BMG plates are joined together successfully. The inclined angles formed by HAZ are between 30 and 80°, determined by the welding power and speed. Lower welding speed or high welding speed corresponds to large angle and shallow penetration. Thus, appropriate welding power and speed provide desired penetration.

Figure 7 shows the SEM images of the polished cross section of the welding joints. Obviously, the welded samples exhibit sound joints without visible welding defects, such as pores or cracks, in both the base material zone and the WFZ (marked area). The whole cross section of the welded joints presents homogeneous structure, meaning the attainment of metallurgical bonding.

In order to characterize the microstructural changes of BMG material, samples 1, 3, 4, and 6 were examined using the transmission electron microscope (TEM). Figure 8 shows the observation results, including the high resolution transmission electron microscope (HRTEM), selected area electron diffraction (SAED) and bright field image (BFI) tests for these samples.

In the base material zone, the HRTEM images (Figure 8a, c, and e) show disorder arrangement of atoms, and the corresponding SAED patterns display clearly that only diffuse halo rings, further proving that the material maintains glassy nature.

In Figure 8b, d, f, and h, the welding power and speed exert a crucial influence on the microstructure of material in the HAZ. For the combined parameters of 3.8 kW and 20 m min⁻¹, serious crystallization happens except very little glass phase present. The average size of crystals is larger than 200 nm. The SAED pattern has visible difference compared with those corresponding to base material. With the increase of welding speed up to 24 m min⁻¹, Sample 3 exhibits fine amorphous structure. Both the HRTEM image and the SAED pattern prove that the material in the HAZ keeps amorphous after rapid scanning of laser beam. The BFI illustrates the glass matrix plus a very few nanocrystals with the size of 40 nm embedded in the marked area. Therefore, it is very appropriate to join Zr₅₅Cu₃₀Al₁₀Ni₅ BMG for the combined parameters of 3.8 kW and 24 m min⁻¹. For the combined parameters of 4 kW and 20 m min⁻¹, the atoms rearrange orderly due to the heat effect from laser scanning. It is no doubt that the material in the HAZ crystallizes completely (see Figure 8f). Along with the speed to 24 m min⁻¹, Sample 6 has obviously different structure compared with sample 4 (Figure 8h). The HRTEM image displays the topological disorder in the most area except the marked zone. The SAED pattern shows the diffuse halo ring with many irregular bright specks, indicating the crystals and amorphous phase coexist. By detection, the BFI shows that some crystals with average
size of 50 nm exist in the glass matrix. Apparently, the nanocrystals appeared, which can improve the mechanical property of materials including hardness, strength, plasticity, etc.\[^{13}\]

As mentioned above, the combined parameters of 3.8 and 4.0 kW with 24 m min\(^{-1}\) are appropriate to join \(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_{5}\) BMG plates. The material remains in glassy state plus few nanoparticles after laser welding. However, the welding power of 3.8 and 4.0 kW with 20 m min\(^{-1}\) lead to rearrangement of atoms. The BMG plates almost crystallize completely. TEM examination is consistent with the Kissinger fitting and simulation of temperature field. Therefore, small welding power or high welding speed should be selected based on full penetration.

4. Conclusions

We use Kissinger analysis and the simulation of temperature field to predict the crystallization of \(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_{5}\) BMG during laser welding, and further to optimize the welding parameters. The CHT curve, temperature field, and thermal cycle curves are obtained and discussed in details. The contours of temperature field on the sample cross section show that the BMG plates are fully penetrated. The material in the base material zone has lower temperature below its crystallization temperature. Combining the CHT curve and the thermal cycle curves, we find that the intersection points exist in the welded samples with low speed or large power, meaning that the crystallization happens in those welding joints.

To validate the Kissinger analysis and temperature field simulation, the laser welding experiments were conducted. The optical microscope results show that the BMG plates are joined together successfully and the workpieces were fully penetrated. The SEM images reveal that the material in the cross section is homogeneous without visible welding defects. Further observation for microstructure changes is completed by TEM. The results show that the welded samples under 20 m min\(^{-1}\) crystallize seriously. With increase of welding speed up to 24 m min\(^{-1}\), the sample with 3.8 kW maintains glassy structure, and the sample with 4 kW has a few nanocrystals embedded in glass matrix. The nanocrystals can improve the mechanical properties of materials. The experimental results are consistent with the simulation, indicating that the Kissinger analysis and simulation of temperature field can be used to predict the crystallization. Therefore, the Kissinger analysis and thermal simulation provide a simple but effective method to analyze the crystallization of BMGs during laser welding, which is beneficial to optimize the welding process.

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Fig. 8. TEM images of the welding joints under different processing conditions. (a), (c), (e), and (g) show the HRTEM images and SAED patterns from base material zone corresponding to samples 1, 3, 4, and 6, respectively. (b), (d), (f), and (h) show the HRTEM images, SAED patterns, and BFI images taken from HAZ corresponding to samples 1, 3, 4, and 6, respectively.
