Effect of Pouring Temperature on Microstructure and Mechanical Properties of Zr-Based Amorphous Alloys

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Abstract. Amorphous alloys possess many excellent physical and chemical properties due to their unique atomic structure. However, owing to the high purity requirement, the production cost of amorphous alloys is often high. In this paper, Zr-based amorphous alloys were prepared from inexpensive industrial raw materials by the copper mold casting method. The effect of pouring temperature on the forming ability and mechanical properties of the alloys was investigated. The results show that at optimized pouring temperature, the glass forming ability as well as the mechanical properties of the alloys can be improved.

1. Introduction
Amorphous material is a type of material in which the atoms and molecules have no long-range symmetry as in crystalline material; instead, they maintain a certain ordered arrangement only in the range of a few atomic layers [1, 2, 3, 4]. Generally, the atomic structure of amorphous alloys has features of short-range order and long-range disorder [5], so that the alloy often has high strength, high hardness [6, 7], high corrosion resistance [8], and excellent magnetic properties [9]. Due to crystal defects, crystalline materials often suffer from disadvantages such as poor resistance to intense mechanical and thermal shock. These shortcomings severely affect the practical applications of crystalline materials in many fields. Amorphous alloys overcome the shortcomings of crystalline alloys, and thus have attracted extensive attention worldwide. In recent decades, amorphous alloys have been widely used in the fields of machinery industry, electronic products, bio-medicine, aerospace, and military [10, 11].

Zr-Al-Ni-Cu alloy system has high glass-forming ability. Its critical cooling rate can be as low as 1 K/s [12], and the super-cooled liquid region is broad. These features all satisfy the requirements for the formation of bulk amorphous alloys. Due to the distinct glass transition ability and a large super-cooled liquid region above 83 K [13], Zr55Al10Ni5Cu30 amorphous alloys are widely used in the fields of military, bio-medicine, etc.

Copper mold casting [14] is one of the most common methods for preparing amorphous alloys. The method has many advantages such as simple equipment setup and easy operation. The key question to the copper mold casting method includes: (1) inhibiting the formation of non-uniform nucleus on the inner wall of the mold; (2) keeping a good state of liquid flow.
One of the challenges in the preparation of amorphous alloys comes from the high purity requirement of the raw materials. If the alloys have incorporation of external impurities, the alloys may crystallize after melting and condensation process, and fail to form amorphous state. However, higher purity of raw materials results in higher production cost, which is unsuitable for large-scale industrial production [15].

For crystalline metals, the pouring temperature is directly related to the casting surface and the defects of the casting [16]. The properties of the amorphous alloys are also related to the pouring temperature. A proper pouring temperature can reduce the effect of casting defects while improving the microstructure and properties of the alloys [17]. In this paper, Zr-based alloy system was selected as the research target. The amorphous alloys were prepared from industrial raw materials by the copper mold casting method. The effect of pouring temperature on the microstructure and properties of Zr-based amorphous alloys were studied.

2. Experimental approach

2.1. Preparation of Zr-based amorphous alloys

The amorphous alloys were prepared using metal blocks with industrial purity. Prior to the experiment, the raw materials were cut into small pieces mechanically. In order to reduce the influence of the raw material purity on the results of the experiments, the surface oxide of the pieces was removed by metal surface treatment.

Table 1. Raw material purity

| Raw material     | Purity (%) |
|------------------|------------|
| Zr (Sponge zirconium) | 99.6       |
| Al               | 99.9       |
| Ni               | 99.9       |
| Cu               | 99.9       |

Next, the raw materials were weighed according to the stoichiometric ratio of Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$ (accuracy to two decimals). The purity of the raw materials is shown in Table 1. To prepare the alloy, the raw materials were first heated in a vacuum induction melting furnace. The vacuum induction melting furnace used electromagnetic induction heating, and the molten metal was stirred constantly with electromagnetic stir bar to ensure the uniformity of the composition. During the experiment, argon protection was used to keep the alloy from oxidation. As the metal melted, the insulation was heated for another half an hour with the heating power adjusted to the minimum. Next, the molten metal was poured into a copper mold to obtain the alloy samples. Finally, the sample weight was compared to the weight of the raw materials to ensure the accuracy of the alloy ratio. The specific operating process is shown in Fig. 1.

![Experimental flow chart of the alloy preparation process](image_url)
By adjusting the power of the vacuum induction melting furnace, the temperature of the molten metal was controlled in different ranges, and alloy samples with different pouring temperatures were obtained. The effect of pouring temperature on the microstructure and properties of samples were then investigated.

2.2. Characterization and property measurement of Zr-based amorphous alloys
The mold casting alloys (thickness of 3 mm) were mechanically crushed to obtain smaller samples. The samples were embedded into a cylindrical specimen holder with a metallographic insert. Next, the sample surface was polished with metallographic sandpaper, followed by hydrochloric and hydrofluoric acid etching. The hardness of the sample was measured using a microhardness tester (MICRO-586). The microstructure of the sample was measured with a metallographic microscope. The phase composition was identified using an X-ray diffractometer (XRD, D8 Advance, and Brucker, Germany) with scan angle from 5 to 70. The morphology of the alloys was measured with a field emission scanning electron microscope (FESEM, Sirion 2000, FEI, and Netherlands).

3. Results and Discussion

3.1. Effect of pouring temperature on the microstructure and properties of the alloys

3.1.1. Effect of pouring temperature on the microstructure of the alloys. For crystalline metals, the pouring temperature directly affects the casting surface and the defects of the casting. For amorphous alloys, the microstructure and properties of the alloys also have an important relationship with the pouring temperature, which is usually reflected on the structure of the alloy melt. In the preparation of amorphous alloys, an effective measure to improve the glass-forming ability is to inhibit the nucleation and growth of the crystals. If heterogeneous nucleation sites exist in the melt, the stability of the supercooled liquid will be reduced, leading to the heterogeneous nucleation of crystals which weakens the glass-forming ability of the alloys. There are two main reasons [18] for the heterogeneous nucleation in the melt. The first reason is the existence of locally ordered atomic clusters, and the second reason is the remaining fine grains at high temperature. Therefore, increasing the pouring temperature can reduce the formation of metastable clusters and the fine grains, enhancing the glass-forming ability of the alloys.

Fig. 2 shows the effect of overly low or high pouring temperature on the morphology of the sample under SEM. As shown in Fig. 2 (a), there are a large number of crystalline structures in the sample obtained at 850°C. This can be attributed to the overly low pouring temperature and the heterogeneous
nucleation caused by the remaining fine grains at high temperature. These heterogeneous nuclei promote crystallization and reduce the glass-forming ability of the alloys. On the other hand, if the pouring temperature is overly high, the melt volume will increase significantly. As the melt is cooled and solidified, the volume shrinkage of the alloy becomes severe, resulting in shrinkage, shrinkage cavity, and other casting defects. Fig. 2 (b) shows that there are apparent shrinkage cavities and other defects on the surface of the sample with pouring temperature of 1200°C.

Fig. 3 shows the effect of pouring temperature on the microstructure of Zr-based amorphous alloys under the metallographic microscope. The sample size was 3 mm, and the magnification was 500 X. The sample was etched with acid before the measurement. All manuscripts must be in English, also the table and figure texts, otherwise we cannot publish your paper. Please keep a second copy of your manuscript in your office. When receiving the paper, we assume that the corresponding authors grant us the copyright to use the paper for the book or journal in question. Should authors use tables or figures from other Publications, they must ask the corresponding publishers to grant them the right to publish this material in their paper.

![Figure 3. Metallographic microscope images showing the effect of pouring temperature on the microstructure of Zr-based amorphous alloys](image)

(a) Pouring temperature is 900°C; (b) Pouring temperature is 1000°C; (c) Pouring temperature is 1100°C

It can be seen clearly from Fig. 3 (a) and Fig. 3 (b) that the alloys have uniform structure with only a few corrosion spots. Fig. 3 (b) shows that the number of corrosion spots is less than that in Fig. 3 (a). However, the corrosion traces in Fig. 3 (c) increase apparently. It is well known that the glass-forming ability of the alloys increases with the increase of the melt temperature in the range of 900°C~1000°C. With the increase of the melt temperature, the heterogeneous nucleation is eliminated. The glass-forming ability is then improved, and the sample shows good corrosion resistance. Nevertheless, overly high pouring temperature can lead to the increase of the melt temperature. During the solidification process, the less efficient heat dissipation may lead to a decrease in the actual cooling rate of the alloys, thus reducing the corrosion resistance of the amorphous alloys system. Therefore, the crystal phase in the alloy precipitates to form a mixed phase. On the other hand, when the oxygen content exceeds a critical value, there is a strong interaction between oxygen and the metal elements. The presence of oxygen promotes the precipitation of the crystalline phase Heating the alloy melt to an excessively high pouring temperature requires longer induction times, which allows the melt to absorb more of the residual oxygen in the working chamber. In addition, if the pouring temperature is overly high, the chemical activity of the alloy melt becomes stronger, and the alloy reacts with oxygen more easily. As a result, the corrosion trace of the alloy sample in Fig. 3 (c) is more obvious compared to samples with pure phase. In order to further determine whether there is crystallization of the alloy, the samples prepared at different pouring temperatures were characterized by XRD, and the diffraction patterns of the alloys were obtained, as shown in Fig. 4.
Figure 4. XRD patterns showing the effect of pouring temperature on the phase composition of Zr-based amorphous alloys

It can be seen from Fig. 4 that there are no obvious sharp peaks in the diffraction patterns of the Zr-based alloys with the same composition prepared at pouring temperature of 900 °C and 1000 °C. These XRD patterns are consistent with the characteristics of the amorphous alloys patterns. The results show that the alloy samples obtained at these two temperatures are basically amorphous alloys. However, in the diffraction pattern of the sample prepared at 1100 °C, sharp peaks begin to emerge, which shows that the crystallization of the alloy is increased, leading to weakened glass-forming ability. The diffraction pattern of the alloy is the same as that of the metallographic structure.

From the above analysis, the effect of pouring temperature on the glass-forming ability of the alloys should be considered from the following three aspects: 1) the existence of locally ordered atomic clusters and the remaining fine grains at high temperature, 2) the actual cooling rate of the alloys, 3) oxygen content. A suitably high pouring temperature can improve the glass-forming ability and reduce the formation of microcrystalline in the preparation of amorphous alloys. However, if the pouring temperature is overly high, the actual cooling rate of the alloy will decrease, leading to mix phase and weakened glass-forming ability of the alloys.

3.1.2. Effect of pouring temperature on the properties of alloys. Hardness is one of the most important mechanical properties of materials. The microstructural behavior of bulk amorphous alloys is often characterized by microhardness. In this work, the hardness of the specimen was measured using MICRO-586 type of microhardness tester. In order to ensure the accuracy of the experimental data, the five points sampling method was employed in the same area of the sample, and the Vickers hardness value was the average of the five sampling points.

Fig. 5 shows the indentation profile (X400) of Zr-based amorphous alloy prepared at 1000 °C. It can be seen that the indentation of the sample is regular diamond shape, which shows that the microstructure of the alloy is uniform.

Figure 5. Indentation image of Zr-based amorphous alloy
Hardness tests were performed on samples casted at 900°C, 1000°C, and 1100°C with the five-point sampling method. The hardness values of Zr-based alloys with different structures were obtained. The results are shown in Table 2.

**Table 2. Hardness measurements of alloys**

| Temperature condition | Hv Mean value |
|-----------------------|---------------|
| 900°C                 | 527.10        |
|                       | 531.32        |
|                       | 531.32        |
|                       | 532.32        |
|                       | 535.60        |
|                       | 531.53        |
| 1000°C                | 539.93        |
|                       | 548.75        |
|                       | 544.31        |
|                       | 539.93        |
|                       | 539.93        |
|                       | 542.57        |
| 1100°C                | 469.33        |
|                       | 469.33        |
|                       | 476.47        |
|                       | 483.77        |
|                       | 465.82        |
|                       | 472.94        |
| Ordinary alloy        | 442.33        |
|                       | 432.79        |
|                       | 426.61        |
|                       | 435.93        |
|                       | 439.11        |
|                       | 435.35        |

Table 2 shows that the Zr-based alloy at 900°C has an average hardness of 531.53, and the hardness of the Zr-based alloy at 1000°C is 542.57. The hardness values of Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$ amorphous alloys are consistent with the reported values in the literature [19].

![Hardness measurements of various samples showing effect of pouring temperature on hardness of Zr-based alloys](image)

**Figure 6.** Hardness measurements of various samples showing effect of pouring temperature on hardness of Zr-based alloys

Fig. 6 shows the effect of pouring temperature on the hardness of Zr-based alloys. It can be seen that the hardness of the ordinary alloy with the same composition are significantly lower. The reason is that the ordinary alloy is mainly composed of crystal structure. The crystalline phase has large amounts of crystal defects such as dislocations. As the pressure is applied, the defects in the crystal structure can cause mechanical properties to deteriorate, resulting in low hardness. The figure shows that suitably high pouring temperature can increase the hardness of the alloy, but the hardness of the alloy may reduce as the pouring temperature become overly high. According to the analysis of the alloy structure from Fig. 4, suitably high pouring temperature can improve the glass-forming ability and increase the amorphous component. Higher amorphous component corresponds to less crystal defects in the structure, leading to better mechanical properties such as higher hardness. However, if the pouring temperature becomes overly high, a large amount of heat in the melt cannot dissipate in time. The cooling rate is reduced, which leads to the increase of the crystalline component and decrease of the alloy hardness. The above results also show that amorphous alloys with the same
composition have apparent different performance from the crystalline alloy, and the amorphous phase can effectively improve the mechanical properties of alloys.

4. Conclusions
Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$ amorphous alloys were prepared from industrial raw materials by the copper mold casting method. The effect of pouring temperature on the microstructure and properties of the Zr-based amorphous alloys was studied. The main conclusions of the paper are summarized as below:

1) The pouring temperature has an important influence on the microstructure and properties of the amorphous alloys. Optimizing the pouring temperature can reduce the nucleation of the alloy liquid during cooling and solidification process, and obtain the amorphous alloys with decent morphology. In the copper mold casting method, as the pouring temperature is in the range of 900°C~1000°C, the glass-forming ability of the amorphous alloys is enhanced with the increase of the melt temperature. As the pouring temperature is higher than 1000 °C, with the increase of the melt temperature, the actual cooling rate of the alloy is reduced, and the amorphous phase is reduced.

2) The amorphous components in the alloy can improve the mechanical property of the alloy. Higher amorphous component in the alloy leads to greater hardness of the alloy. The average hardness value of the amorphous alloys prepared by the copper mold casting method is about 540, which is well above the hardness of the crystalline alloys with the same composition.

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References
[1] Inoue A, Takeuchi A, Recent development and application products of bulk glassy alloys, Acta Materialia, 59 (2011) 2243-2267.
[2] Zallen R, The physics of amorphous solids, Wiley Online Library, 1983.
[3] Wang Weihua, The nature and properties of amorphous mater, Progress in Physics, 33 (2013) 177-351.
[4] Lu Z P, Liu C T, A New Glass-forming Ability Criterion for Bulk Metallic Glasses, Acta Materialia, 50 (2012) 3501-3512.
[5] Guo Yuqin, Li Fuzhu, Yang Xin, Han Juanjuan, Review on BMGs research and progress in the past decade, Journal of Materials Science and Engineering, 29 (2011) 806-810.
[6] Challapalli Suryanarayana, Mechanical behavior of emerging materials, Materials Today, 15 (2012) 486-498.
[7] Xue Peng, Mechanical behaviors of a ZrAlNiCu bulk metallic glass, Harbin Institute of Technology, Harbin, 2016.
[8] Yang B, Du Y, Liu Y, Recent progress in criterions for glass forming ability, Transactions of Nonferrous Metals Society of China, 19 (2009) 78-84.
[9] Iqbal M, Akhter J I, Zhang H F, Hu Z Q, Synthesis and mechanical properties of Zr-based bulk amorphous alloys, Journal of Non-Crystalline Solids, 354 (2008) 3291-3298.
[10] Inoue A, Bulk Glassy Alloys: Historical Development and Current Research, Engineering, 1 (2015) 185-191.
[11] Li H F, Zheng Y F, Recent advances in bulk metallic glasses for biomedical applications, Acta Biomaterialia, 36 (2016) 1-20.
[12] Yang Ke, Preparation and properties of Cu-based bulk metallic glass, Xi’an Technological University, Xi’an, 2014.
[13] Inoue A, Zhang T, Chen M W, Sakurai T, Formation and properties of Zr-based bulk quasicrystalline alloys with high strength and good ductility, Journal of Materials Research, 15 (2000) 2195-2208.
[14] Pi Jinhong, Zhuang Huwen, Ni Jiajia, et al, Review on synthesis of bulk metallic glasses,
[15] Chen Chen, Yangyang Cheng, Tao Zhang. Synthesis of impurity-insensitive Zr-based bulk metallic glass, Journal of Non-Crystalline Solids, 439 (2016) 1-5.
[16] Pang Song, Wu Guohua, Liu Wencai, Influence of pouring temperature on solidification behavior, microstructure and mechanical properties of sand-cast Mg_{10}Gd_{3}Y_{0.4}Zr alloy, Transactions of Nonferrous Metals Society of China, 25 (2015) 363-374.
[17] Liu Guangqiao, Kou Shengzhong, Li Chunyan, et al, Effects of pouring temperature on GFA and mechanical properties of Zr-based bulk metallic glass, Foundry, 60 (2011) 441-446.
[18] Hu Zhuangqi, Zhang Haifeng, Recent progress in the area of bulk amorphous alloys and composites, Acta Metallurgica Sinica, 46 (2010,) 1391-1421.
[19] He Qingkun, Liu Juncheng, Wang Jin, et al, Preparation and properties of Zr_{55}Al_{10}Ni_{5}Cu_{30} amorphous alloy, Nonferrous Metals, 9 (2013) 60-62.