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A study of the glass forming ability in ZrNiAl alloys

Q. Jing [a,b,*], Y. Zhang [a], D. Wang [a], Y. Li [a]

[a] *Department of Material Science and Engineering, National University of Singapore, Singapore 117576, Singapore*
[b] *Key Laboratory of Metastable Material Science & Technology, Yanshan University, PR China*

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Abstract

The melting and solidification behavior of ZrNiAl alloys were studied. Near one eutectic point, several alloys were found exhibiting a good glass forming ability (GFA) and amorphous rods of 2, 5 and 8 mm in diameter were cast. $Zr_{60}Ni_{21}Al_{19}$ alloy was found to exhibit excellent GFA and amorphous rods with 8 mm in diameter were successfully cast. All the alloys exhibit the same melting temperature, which indicates that they belong to the same ternary eutectic system.

Keywords: Zr based alloys; Bulk metallic glass; Eutectic; Glasses forming ability

1. Introduction

Since early 1990s great progress has been made in research on bulk metallic glasses (BMGs). Many bulk metallic glass systems have been developed, which offer great potential for commercial applications [1–4]. Of these BMGs systems Zr based bulk metallic glasses exhibit excellent properties. The multi-component Zr based Be containing alloys are the most commercially available bulk metallic glasses. They exhibit excellent mechanical properties. Their strength can be as high as 2 GPa, and elastic strain is approximately 2%, which are substantially higher than those of the most crystalline alloys. One of the most highly processible BMGs is alloy $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$, which has a critical cooling rate of about 1 K/s [5]. But this BMG alloy has not been applied widely because Be is highly toxic, particularly in the gaseous form. There is a need to replace Be containing Zr based alloys with non-Be containing ones, for either as the monolithic bulk metallic glasses or as the matrix for the bulk metallic glass composite. As many BMGs have been reported in the Zr–Cu–Ni–Al alloys [6,7], it would be useful to study the Zr–Ni–Al system [8–11] as the starting point for further investigation in high order multi-component systems. In this paper glass forming ability (GFA) of the ternary Zr–Ni–Al alloys was studied and the amorphous rods of 8 mm in diameter were successfully prepared.

2. Experimental

The ZrNiAl alloy ingots were prepared by arc melting metals of Zr (99.98%), Ni (99.98%) and Al (99.9%) together in Ti-gettered argon atmosphere. Before melting, the vacuum level in the furnace reached 10^{-3} Pa. Each of the ingots was melted six times to ensure uniformity in composition. Melting and solidification studies of the ZrNiAl alloys were carried out in a differential thermal analyzer (DTA) at a heating and cooling rate of 20 K/min using a TA instrument. The ZrNiAl alloy samples with different compositions were sealed in quartz tubes to prevent oxidation during heating. The alloys were cast into cylindrical copper moulds, 2, 5, or 8 mm in diameter. The resulting samples were then sectioned transversely, etched and then observed by optical microscopy. Differential scanning calorimetry (DSC) experiments were carried out at a heating rate of 20 K/min using the TA instrument. XRD experiments were also carried out with Cu Kα radiation using a Philips X'Pert X-ray diffraction instrument to verify the amorphous and crystalline states of the samples.

3. Results and discussion

Alloys with excellent GFA are usually found around the eutectic composition [12] and eutectic compositions can be

* Corresponding author at: College of Material Science and Engineering, West Campus of Yanshan University, Qinhuangdao, Hebei 066004, PR China, Tel.: +86 335 8064504; fax: +86 335 8064504.
E-mail address: jingqin@ysu.edu.cn (Q. Jing).

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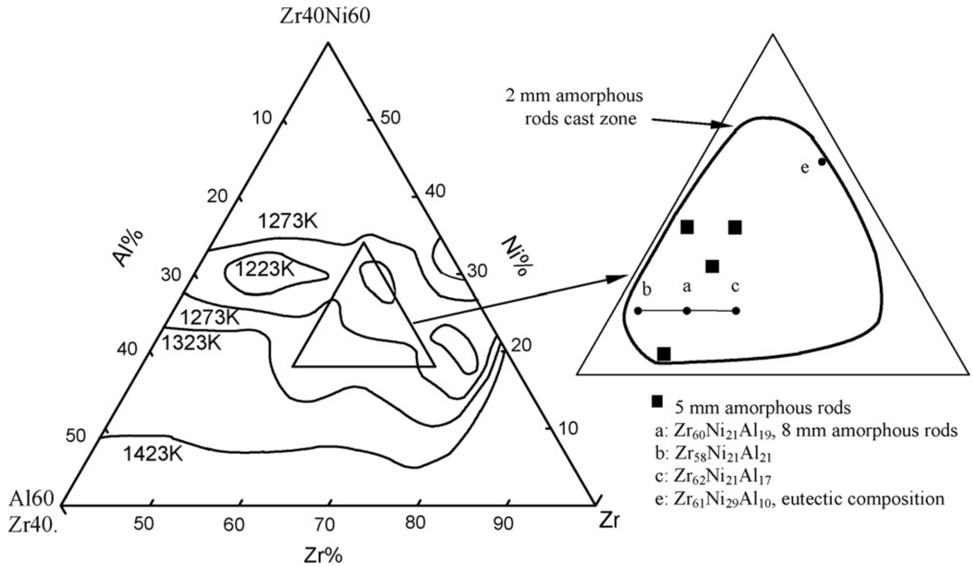

Fig. 1. T_l temperatures and composition range in which 2, 5 and 8 mm amorphous rods cast.

located by studying the melting and solidification behaviors of the alloys. A eutectic alloy exhibits only one eutectic transformation during melting and cooling. Moreover alloys near a eutectic point always have the same onset melting temperature (T_m). To find the ternary eutectic points in the Zr rich ZrNiAl alloys, the melting behaviors of some ZrNiAl alloys have been studied by means of DTA experiment. Their liquidus temperatures (T_l) are plotted in Fig. 1. Of these alloys, alloys $Zr_{46}Ni_{30}Al_{24}$, $Zr_{61}Ni_{29}Al_{10}$ and $Zr_{74}Ni_{20}Al_6$ exhibit relatively low T_l temperatures compared with those of the surrounding alloys. During melting only one melting peak, corresponding to the eutectic melting, can be observed in the DTA results. Thus they should be very near to their respective eutectic composition points. DTA results of alloy $Zr_{61}Ni_{29}Al_{10}$ are shown in Fig. 2 showing only one melting peak.

The GFA of the alloys in these three eutectic systems were studied, and the alloys in the $Zr_{61}Ni_{29}Al_{10}$ eutectic system were found to have good GFA. Fig. 3 shows the XRD results of the 2 mm rods cast from the alloys in this eutectic system. No crystalline peaks could be found on the patterns. The DTA results shown in Fig. 4 indicate that all these alloys exhibit the same T_m temperature, which means that they are indeed in the same eutectic system. The DSC results on cooling the rods of 2 mm in diameter are shown in Fig. 5 and exhibit obvious exothermic peaks. XRD results in Fig. 6 indicate that some of these alloys could be cast into amorphous rods of 5 mm in diameter, and fur-

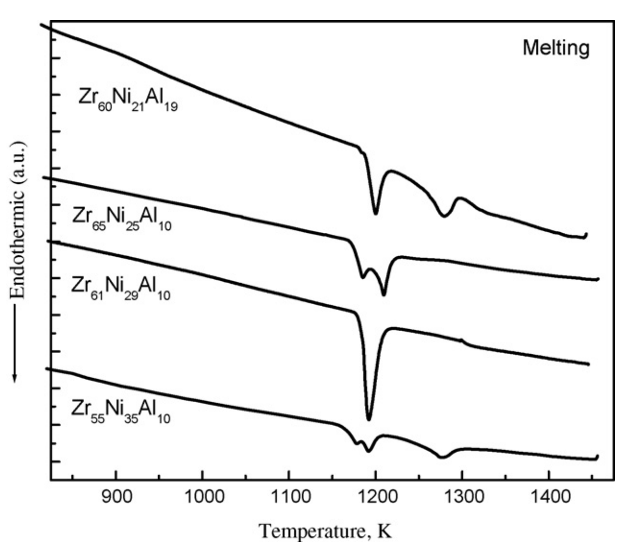

Fig. 2. DTA results of the ZrNiAl alloys at 10 at.%Al.

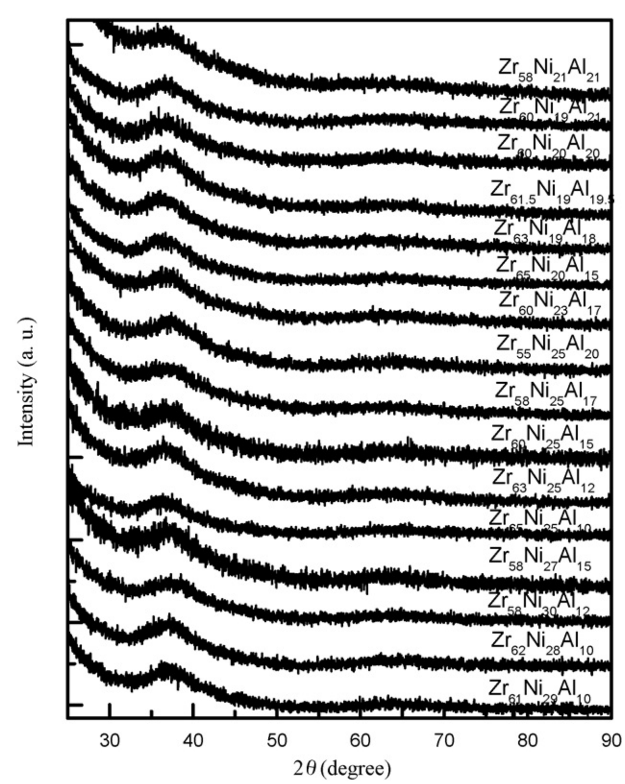

Fig. 3. XRD results of the rods 2 mm in diameter.

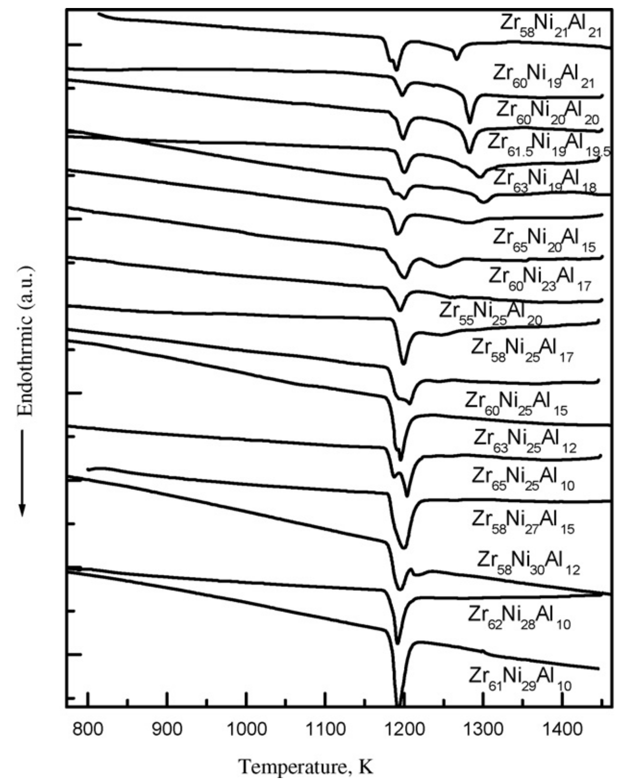

Fig. 4. DTA results of the ZrNiAl alloys shown in Fig. 3.

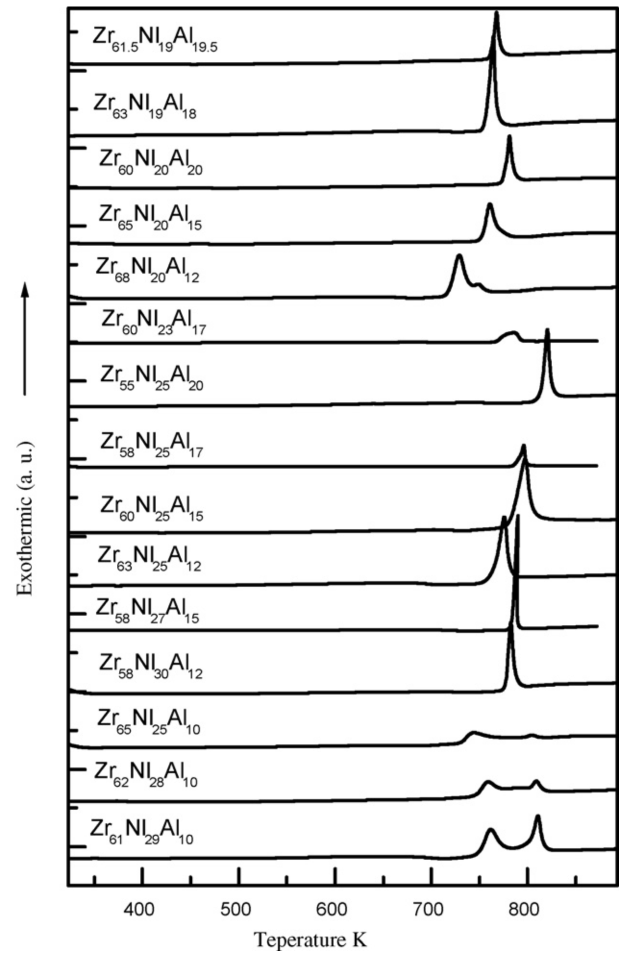

Fig. 5. DSC results of the ZrNiAl alloys shown in Fig. 3.

thermore XRD results in Fig. 7 confirm that alloy $Zr_{60}Ni_{21}Al_{19}$ exhibits the best GFA and no crystalline peaks could be found on its XRD pattern of the 8 mm diameter rod indicating a full of amorphous state of the sample within the sensitivity of the XRD.

From the DTA results shown in Fig. 2, one can see that alloy $Zr_{60}Ni_{21}Al_{19}$ is an off-eutectic alloy. The XRD result of the 3 mm cast rod of the eutectic alloy $Zr_{61}Ni_{29}Al_{10}$ is shown in Fig. 8, and obvious crystalline peaks can be observed in the pattern. Thus the eutectic alloy $Zr_{61}Ni_{29}Al_{10}$ can only be cast into amorphous rods of 2 mm in diameter, in contrast to the off-eutectic alloy $Zr_{60}Ni_{21}Al_{19}$ which can be cast into amorphous rods of 8 mm in diameter. Therefore, the alloy with the best GFA is not at the eutectic composition. The composition range in which amorphous rods of 2, 5 and 8 mm could be cast is summarized in Fig. 1. It should be noted that the best glass forming alloy, $Zr_{60}Ni_{21}Al_{19}$, is different from that in the ZrCuAl alloy system. In the ZrCuAl system the alloys with good GFA, which can be cast into 8 mm amorphous rods contain no more than 8 at.% Al [13], while the best alloy in the ZrNiAl system has 19 at.% Al. Nevertheless both results of 8 mm amorphous rods in the ZrCuAl and ZrNiAl systems are excellent developments because they are simple ternary alloy systems. Based on these results other elements can be added to achieve even larger sized bulk metallic glasses as it has been reported that excellent glass forming alloys can be found in multi-component alloys.

Eutectic transformation is very important to GFA of alloys [14]. In fact most BMG alloys are around a eutectic composition. There are two types of eutectic phase systems in terms of their coupled zone defining the composition and growth temperature (undercooling) range that leads to entirely eutectic growth. One is symmetrical about the eutectic composition, and the other is skewed. Whether an alloy solidifies to eutectic or primary crystal in a eutectic matrix would depend on competitive growth between the primary phase and eutectic phases. On cooling the phase transformation is governed by growth temperature and

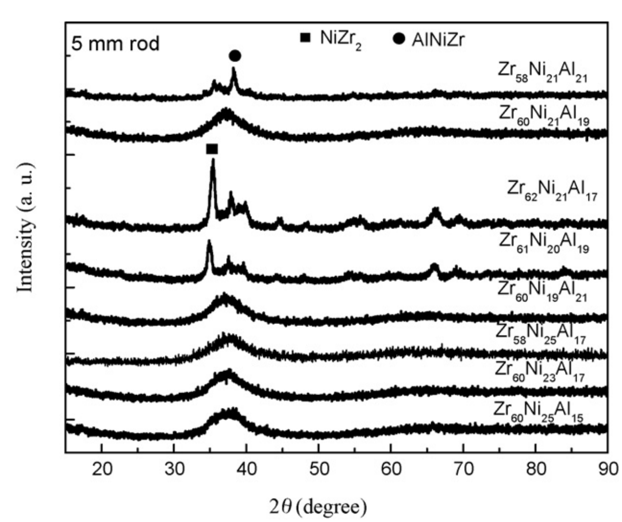

Fig. 6. XRD results of the rods 5 mm in diameter.

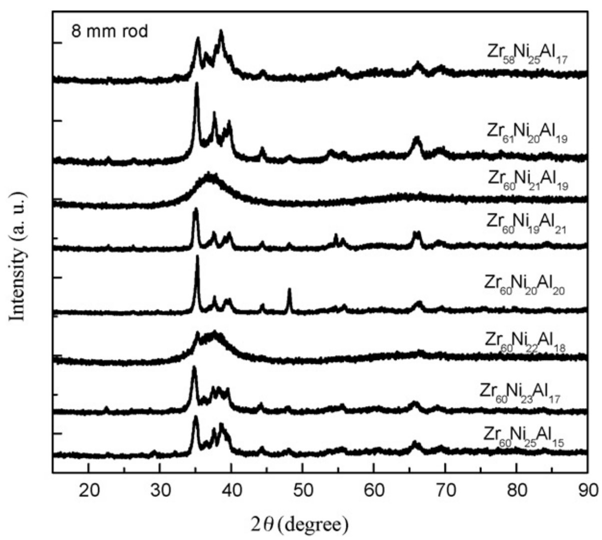

Fig. 7. XRD results of the rods 8 mm in diameter.

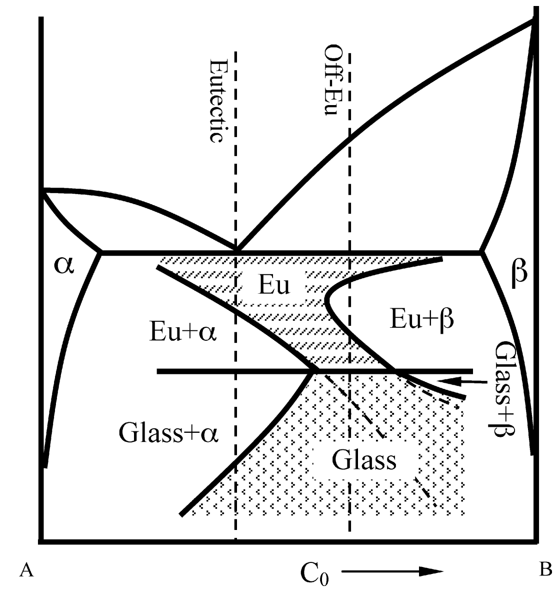

Fig. 9. Skewed eutectic coupled zone and glass forming zone.

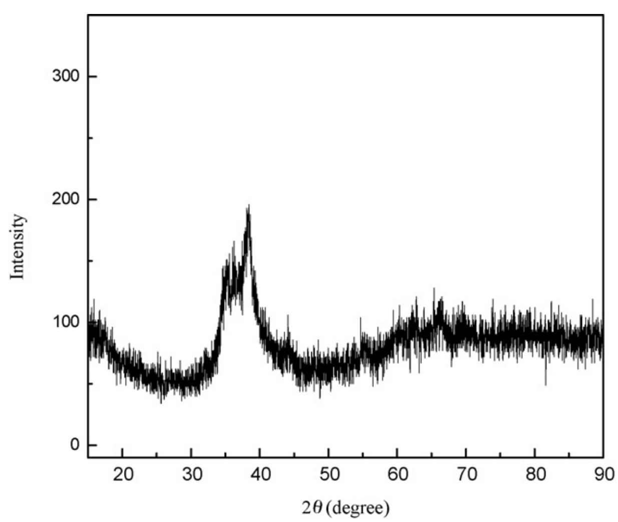

Fig. 8. XRD result of 3 mm rod cast from alloy $Zr_{61}Ni_{29}Al_{10}$.

composition of alloys. In the eutectic system suppressing primary phase transformation is more difficult than suppressing eutectic transformation on cooling. Thus sometimes composites with metallic glass matrix and primary metallic phases can be prepared [15–18]. Therefore in the eutectic system with skewed coupled zone, shown in Fig. 9, full glass is formed in off-eutectic alloys. This is the reason why the off-eutectic alloy $Zr_{60}Ni_{21}Al_{19}$ show a better GFA than the eutectic alloy $Zr_{61}Ni_{29}Al_{10}$. The idea has been successfully confirmed in Zr–Cu–Al [13], Zr–Cu [14], La–Al–Cu–Ni [19], and Pr–Cu–Ni–Al [20] bulk metallic glass systems. From Fig. 10 it can be seen that there are very little isolated eutectic crystalline regions, about 2.7% in the etched section, can be found in the glass matrix in the 8 mm rod cast from alloy $Zr_{60}Ni_{21}Al_{19}$, which means that it is eutectic forming alloy under deep undercooling though it exhibit an off-eutectic alloy solidification behavior in Fig. 2. Micrographs of the etched cross-sections of the 5 mm rods cast from alloy $Zr_{58}Ni_{21}Al_{21}$ and $Zr_{62}Ni_{21}Al_{17}$ are shown in Fig. 11, whose compositions are excursions from the best alloy $Zr_{60}Ni_{21}Al_{19}$

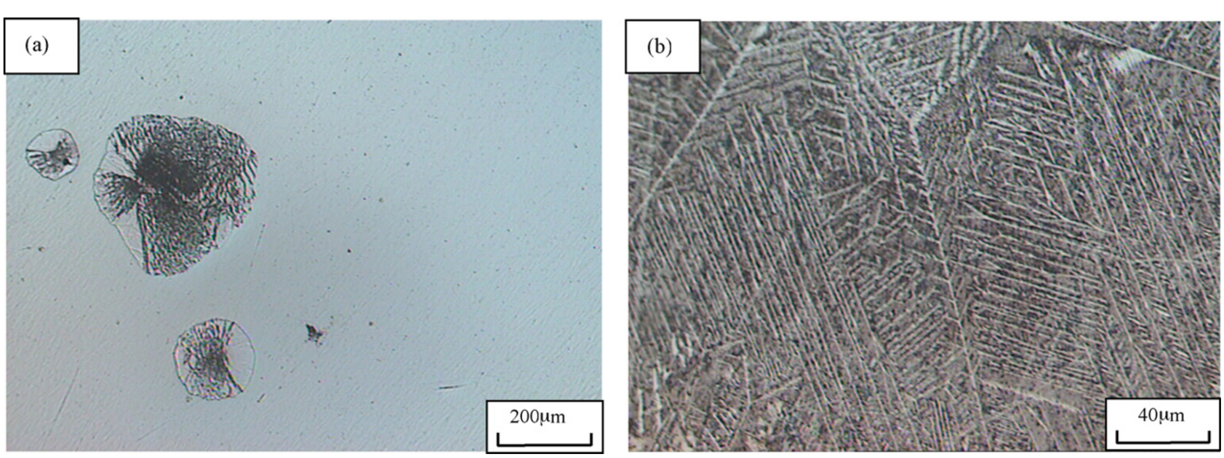

Fig. 10. The eutectic in 8 mm rods cast from alloys $Zr_{60}Ni_{21}Al_{19}$: (a) the eutectic on the glass matrix and (b) the center of the eutectic.

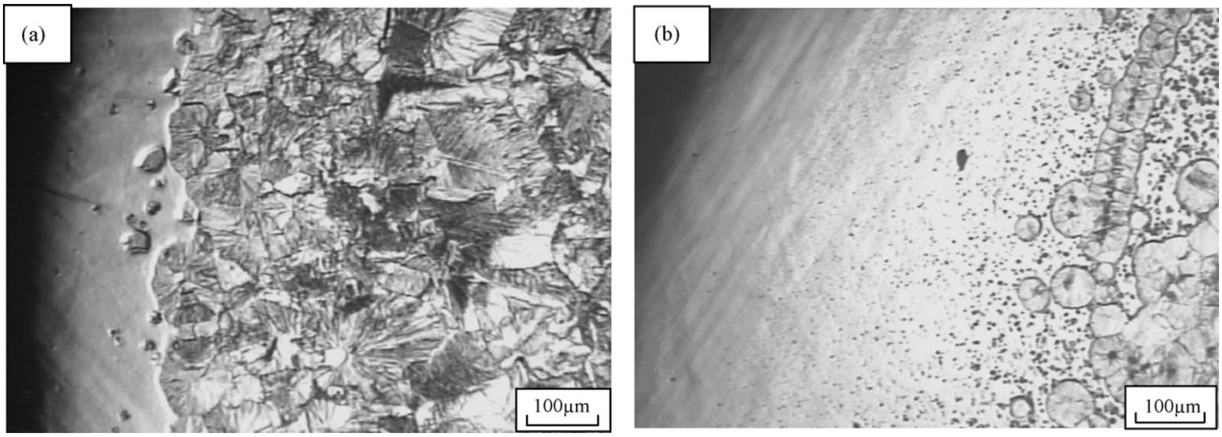

Fig. 11. Micrographs of the etched cross-sections of the 5 mm rods cast from alloys: $Zr_{62}Ni_{21}Al_{17}$ (a) and $Zr_{58}Ni_{21}Al_{21}$ (b).

with element Zr added or reduced (shown in Fig. 1), and whose GFA is not as good as alloys $Zr_{60}Ni_{21}Al_{19}$. From the XRD results shown in Fig. 6 one can see that the main crystalline phase in the $Zr_{58}Ni_{21}Al_{21}$ rod is the compound AlNiZr, and the main crystalline phase in the $Zr_{62}Ni_{21}Al_{17}$ rod is the compound $NiZr_2$.

Turnbull focused on the conditions for suppressing nucleation to the undercooling required for reaching the glass state [21]. He considered that these are the most important conditions for forming glass from liquids which are quite fluid at their melting temperature. According to the conditions, liquids with T_{rg} as high as 1/2 could be chilled to the glass state in relatively small volumes and at high cooling rates. However, we suggest that the growth of crystalline nuclei is also very important to glass formation. Some small crystalline phases have been found in many amorphous samples, which means that the nucleation was not suppressed, but the growth was limited. The eutectic crystals could be found in 8 mm samples cast from alloys $Zr_{60}Ni_{21}Al_{19}$, shown in Fig. 10, though the sample exhibits amorphous XRD patterns. Large amount of small crystalline phases can be found in the etched section of the sample cast from alloy $Zr_{60}Ni_{23}Al_{17}$ shown in Fig. 12(a), but the matrix is still amorphous in the area shown. In Fig. 12(b) though heterogeneous nucleation occurred on the wall of the mould, the crystalline phases only grow in a very narrow zone at the edge of the ingot and amorphous phase formed in the remainder. Thus suppressing the growth of crystal nuclei is very beneficial to the glass formation.

T_{rg} [21], ΔT_x [22], γ [23] and other indicators [1,11,24,25] are often used to evaluate the GFA of alloys and many bulk metallic glasses were successfully found with the help of these indicators [5,26–29]. But there are also some excellent BMGs which are not consistent with these indicators. The thermal properties of the alloys which can be cast into amorphous 2 mm rods, are summarized in Table 1. The value ranges of T_{rg}, ΔT_x and γ of the alloys are between 0.53 and 0.58, 32.2 and 61.4, and 0.37 and 0.39, respectively. Their average values are 0.557, 44.36 and 0.38, respectively. The literature [21] suggested that an alloy exhibits a good GFA when its T_{rg} is larger than 0.5. According to the literature [23] BMG alloys should have a γ larger than 0.35. All the alloys in Table 1 have T_{rg} larger than 0.53 and γ larger than 0.37. They exhibit good GFA and 2 mm rods were cast successfully. From the XRD patterns in Figs. 6 and 7 alloys $Zr_{60}Ni_{21}Al_{19}$ and $Zr_{60}Ni_{22}Al_{18}$ exhibit better GFA. Their T_{rg}, ΔT_x and γ values are between 0.55 and 0.56, 43.3 and 46.5 and 0.38, respectively. These values are not the highest ones in

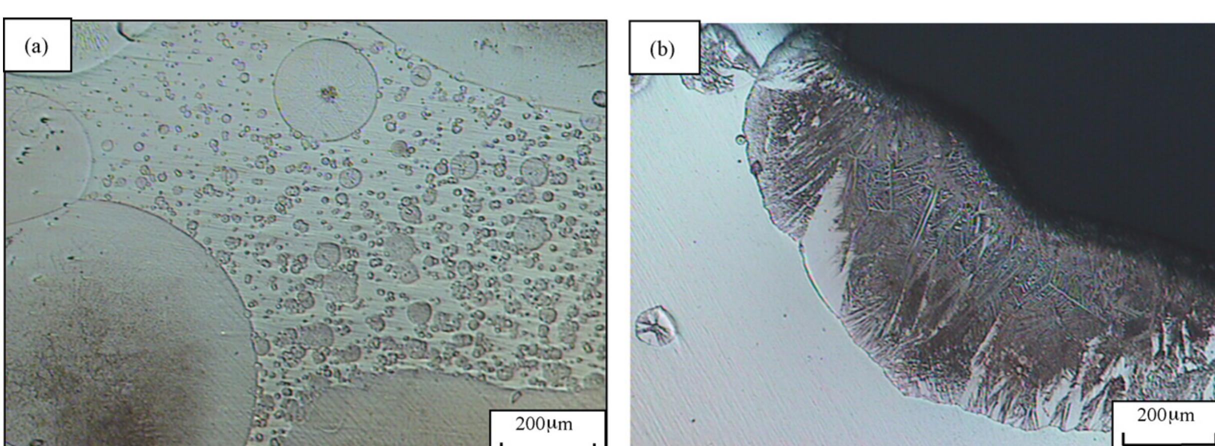

Fig. 12. Crystalline and amorphous phases in the samples: (a) alloy $Zr_{60}Ni_{23}Al_{17}$ and (b) alloy $Zr_{61}Ni_{20}Al_{19}$.

Table 1
Thermal properties of the ZrNiAl bulk metallic glasses

	T_g (K)	T_x (K)	T_m (K)	T_l (K)	ΔT_x (K)	T_{rg}	γ
$Zr_{61}Ni_{29}Al_{10}$	697.5	738.6	1179.8	1210.6	41.1	0.58	0.39
$Zr_{62}Ni_{28}Al_{10}$	696.5	736.1	1177.2	1218.3	39.6	0.57	0.38
$Zr_{58}Ni_{30}Al_{12}$	717.9	769.1	1178.9	1233.5	51.2	0.58	0.39
$Zr_{58}Ni_{27}Al_{15}$	724.9	–	1179.4	1274.2	–	0.57	–
$Zr_{65}Ni_{25}Al_{10}$	681.7	721.7	1177	1253	40	0.54	0.37
$Zr_{63}Ni_{25}Al_{12}$	691.3	744.9	1180	1219.1	53.6	0.57	0.39
$Zr_{60}Ni_{25}Al_{15}$	715.4	770.2	1179	1261.4	54.8	0.57	0.39
$Zr_{58}Ni_{25}Al_{17}$	728.8	790.2	1185.0	1303	61.4	0.56	0.39
$Zr_{55}Ni_{25}Al_{20}$	757.1	803.3	1177.5	1247.2	46.1	0.56	0.38
$Zr_{60}Ni_{23}Al_{17}$	715.8	767.1	1179.0	1279.6	51.3	0.56	0.38
$Zr_{62}Ni_{21}Al_{17}$	706.4	751.1	1179.6	1304.4	44.7	0.54	0.37
$Zr_{61}Ni_{21}Al_{18}$	714.4	759.7	1176.4	1292.3	45.3	0.55	0.38
$Zr_{60}Ni_{21}Al_{19}$	723.0	766.4	1184.9	1295.1	43.4	0.56	0.38
$Zr_{65}Ni_{20}Al_{15}$	695.3	741.7	1179.1	1306.2	46.4	0.53	0.37
$Zr_{61}Ni_{20}Al_{19}$	717.1	758.7	1176.4	1304.0	41.6	0.55	0.38
$Zr_{63}Ni_{19}Al_{18}$	706.0	745.2	1178.5	1314.2	39.2	0.54	0.37
$Zr_{61.5}Ni_{19}Al_{18.5}$	721.0	756.3	1186.5	1318.2	35.3	0.55	0.37
$Zr_{60}Ni_{20}Al_{20}$	730.3	768.9	1178.9	1354.7	38.6	0.54	0.37
$Zr_{60}Ni_{19}Al_{21}$	731.6	763.8	1185.3	1299.8	32.2	0.56	0.38
$Zr_{60}Ni_{22}Al_{18}$	720.1	766.6	1181.9	1289.9	46.5	0.56	0.38
$Zr_{58}Ni_{21}Al_{21}$	744.3	779.1	1173.9	1337.2	34.8	0.56	0.38

Table 1, and are near the average values of the indicators. Thus T_{rg}, ΔT_x and γ are not very sensitive to the GFA of the ZrNiAl alloys in critical size from 2 to 8 mm.

4. Conclusion

In conclusion, some alloys around $Zr_{60}Ni_{21}Al_{19}$, which have the same T_m temperature and belong to the same eutectic system, were found to have good GFA. $Zr_{60}Ni_{21}Al_{19}$ bulk amorphous alloy rods with a diameter of 8 mm were successfully prepared. T_{rg} and γ can predict the good GFA of the ZrNiAl alloys, but they are not very sensitive to the GFA of the ZrNiAl alloys in critical size from 2 to 8 mm.

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