A Novel Ni-Free Zr-Based Bulk Metallic Glass with High Glass Forming Ability, Corrosion Resistance and Thermal Stability

Yu Luo, Yidong Jiang, Pei Zhang, Xin Wang, Haibo Ke and Pengcheng Zhang*

Abstract

Zr-based Bulk metallic glasses exhibit incredible corrosion resistance and glass forming ability, however, these properties need further enhancement to meet the practical use. In this study, Zr_{63}Fe_{2.5}Cu_{23}Al_{11.5}, a new type of Zr-based bulk metallic glass was fabricated. Potentiodynamic polarization techniques were used to measure the corrosion resistance of this alloy. Furthermore, crystallization behavior and kinetics of Zr_{63}Fe_{2.5}Cu_{23}Al_{11.5} bulk metallic glass were investigated by using differential scanning calorimetry of non-isothermal model. Kissinger and Ozawa methods were used for calculating activation energies of crystallization and the mechanism of crystallization was analyzed by Johnson-Mehl-Avrami-Kolmogorow methods. The results suggest that this specified metallic glass system possesses a relatively high thermal stability and glass forming ability. Moreover, the crystallization procedure is mainly dominated by nucleation with an increasing rate. The study demonstrates that the slight composition adjustment of Zr–Fe–Cu–Al system bulk metallic glass can make a considerable contribution to higher glass forming and thermal stability as well as corrosion resistance.

Keywords: Zr-based BMG, Glass forming ability, Corrosion resistence, Thermal stability, Crystallization behavior

1 Introduction

Zr-based BMGs have drawn an increasing attention in recent years for their unique properties, such as high hardness, superior strength, excellent fracture toughness, enhanced elastic limit as well as improved corrosion resistance [1, 2]. As strongly potential materials in biomedical industries, most of the Zr-based BMGs contain Ni or Be elements, which may cause allergies in human body [3]. Then Zr_{60}Fe_{10}Cu_{20}Al_{10}, a developed Zr-based Ni-free alloy is proposed for substitution, which possesses rather good glass forming ability (GFA) [4]. However, limited GFA is a major restriction in the application of BMGs as structural materials. Composition adjustment is therefore used to improve the GFA of BMGs [5, 6].

BMGs are essentially metastable, which inherently has the possibility to crystallize into a stable structure during thermal variation [7, 8]. To build practical BMG parts, hot forming during super-cooled liquid region is often employed [9], the occurrence of partial crystallization may take place because of the thermal effect. Generally, the corrosion resistance of Zr-based bulk metallic glasses (BMGs) with amorphous structure is 1–2 orders of magnitude higher than their crystalline counter parts, for the lacking of structural defects such as dislocations or grain boundaries in BMGs [10–13]. Thus, the building up of high performance BMG parts calls for a good thermal stability of BMGs to avoid the formation of crystalline phases. Therefore it is of great significance to recognize both the thermal characteristics and crystallization processes. The understanding of crystallization from kinetic aspect is important since the competition between nucleation and growth during the generating of crystalline phase can be quantified through the kinetic characters.
investigated by non-isothermal DSC methods. In particular, the 
Zr63Fe2.5Cu23Al11.5 specimens tested to 838 K under heating rates of 10, 20, 40 and 80 K/min, 
carried out within the temperature ranging from 300 K
2.3  Thermal Behavior and Crystallization Kinetics
The differential scanning calorimetry (DSC) tests were 
acquired by X-ray diffraction (XRD, Philips X’Pert Pro) 
using Cu–Kα radiation with the determine range from
20° to 90°. Before the measurement, the cylindrical rods 
were cut into pieces with the height of 1 mm and the 
cross section of the rods were grind by abrasive paper 
then polished on a polishing cloth with diamond polishing 
agent. The diffraction profiles were used to evaluate 
the thermal stability and crystallization behavior of 
Cu47Zr53Al and (Cu47Zr53Al)50Sn50 bulk metallic glasses.
In this work, Zr63Fe2.5Cu23Al11.5 BMG, a new type of 
Zr–Fe–Cu–Al system BMG with better glass forming 
ability and thermal stability, was prepared by suction- 
casting method. The corrosion resistance of the 
Zr63Fe2.5Cu23Al11.5 BMG was tested by potentiody-
namic polarization techniques and then compared to 
Zr60Fe10Cu20Al10 BMG, 316L stainless steel (traditional 
structure material) as well as Ti-6Al-4V alloy (pitting 
resistant structural material). The thermal stability and 
crystallization kinetics of Zr63Fe2.5Cu23Al11.5 alloy were 
investigated by non-isothermal DSC methods. In particular, 
the crystallization kinetics were illuminated by studying 
the crystallization activation energy and crystallization 
mechanism.

2 Experiments
2.1 Materials Preparation
To avoid adding superfluous elements, the master in-
gots with nominal composition of Zr60Fe10Cu20Al10 (in at%) 
and Zr63Fe2.5Cu23Al11.5 (in at%) were fabricated by using arc-melting high-purity ingots of Zr (>99.9 wt%), Fe 
(>99.99 wt%), Cu (>99.9 wt%) and Al(99.99 wt%) for 
four times at least to ensure the chemical homogeneity. 
And cylindrical rods in diameters of 1–14 mm were 
fabricated under Ar atmosphere by suction-casting in water-
cooled copper molds.

2.2 X-ray Diffraction Measurement
The structural information of the as-cast rods were 
acquired by X-ray diffraction (XRD, Philips X’Pert Pro) 
using Cu–Kα radiation with the determine range from
20° to 90°. Before the measurement, the cylindrical rods 
were cut into pieces with the height of 1 mm and the 
cross section of the rods were grind by abrasive paper 
then polished on a polishing cloth with diamond polishing 
agent. The diffraction profiles were used to evaluate whether the as-cast rods were in an amorphous status.

2.3 Thermal Behavior and Crystallization Kinetics
 Measurement
The differential scanning calorimetry (DSC) tests were 
carried out within the temperature ranging from 300 K 
to 838 K under heating rates of 10, 20, 40 and 80 K/min, 
respectively. The Zr63Fe2.5Cu23Al11.5 specimens tested 
in DSC were thinned before loading in the DSC cells to 
ensure the accuracy of the test.

2.4 Corrosion Test
The as-cast rods of Zr63Fe2.5Cu23Al11.5 alloy with diam-
eters of 5 and 6mm and the Zr60Fe10Cu20Al10 alloy with 
diameters of 1 and 3mm were cut into pieces, and then 
fixed in epoxy resin and the untested side of speci-
mens were linked with copper wires. These specimens 
were mechanically polished by an automated lapping 
machine, then sonicated in anhydrous alcohol for 600 s 
and sequentially dried by Ar flow. The corrosion behav-
ior of Zr63Fe2.5Cu23Al11.5 samples were characterized by 
potentiodynamic polarization techniques which were 
conducted on an electrochemical workstation (AutoLab 
302N, Metrohm). A three-electrode system was consis-
t of a Zr63Fe2.5Cu23Al11.5 working electrode, a 4 cm² Pt net as the counter electrode and a saturated calomel 
electrode as the reference electrode. The electrolyte was 
NaCl solution (3.5 wt%), and the electrolytic cell was 
commercial flat electrolytic cell. For comparison, the cor-
rosion resistance of Zr60Fe10Cu20Al10 316L stainless steel 
and Ti-6Al-4V alloy were tested as well.

3 Results and Discussion
3.1 Glass Forming Abilities of Zr–Fe–Cu–Al BMGs
Figure 1 exhibits the XRD results of cylindrical 
rods in different diameters of Zr60Cu20Fe10Al10 and 
Zr63Fe2.5Cu23Al11.5 alloys. Due to the instrument we 
used in the present work, the critical diameter of 
Zr60Cu20Fe10Al10 BMG is 1 mm (Figure 1a), while the critical diameter of Zr63Fe2.5Cu23Al11.5 BMG is 5 mm (Fig-
ure 1b), which shows that the GFA of Zr63Fe2.5Cu23Al11.5 
BMG is much better than that of Zr60Cu20Fe10Al10. 
The results indicate that Zr63Fe2.5Cu23Al11.5 BMG may 
have extensive application prospect compared with 
Zr60Cu20Fe10Al10 BMG in building practical parts.

3.2 Corrosion Resistance of Zr63Fe2.5Cu23Al11.5 BMG
Zr63Fe2.5Cu23Al11.5, Zr60Fe10Cu20Al10 BMGs, 316L stainless 
steel and Ti–6Al–4V alloy in 3.5% NaCl solution are 
illustrated in Figure 2, and corresponding corrosion data 
are listed in Table 1. It can be seen that all the Zr-based 
BMGs exhibit better corrosion performance than tradi-
tional structural materials (316L). With respect to Zr-
based BMGs with the same composition, the presence of 
a small amount of crystals leads to an order of magnitude 
increase in corrosion rate than that of amorphous phase.
In addition, slightly composition adjustment can change 
the corrosion resistance of Zr-based BMGs to some 
extent. With the decrease of the composition of Fe from 
10 at.% to 2.5 at.% in Zr–Fe–Cu–Al BMG, the corro-
sion potential (Ecorr) increases and the corrosion current
density ($I_{corr}$) reduces 80%, indicating that the corrosion resistance of the Zr–Fe–Cu–Al BMGs is improved significantly. It is worth noting that the corrosion resistance of Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ reaches the level of structural materials (Ti-6Al-4V alloy). It is mainly due to the reduction of amorphous material defects and the absence of grain boundaries.

3.3 Thermal Stability of Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ BMG

Figure 3 shows typical non-isothermal DSC curves measured from the Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ BMG under different heating rates. All the curves exhibit a single exothermic peak. The corresponding transition temperatures of inner structural, including glass transition temperature ($T_g$), crystallization temperature ($T_x$), and peak temperature ($T_p$), are listed in Table 2. It can be seen from Table 2 that with the increasing of heating rate, all the temperatures move to a higher value, which is characteristic of a dominant kinetic process. The curves show extended super-cooled liquid regions $\Delta T_p$ of width 76-86K, which are close to the reported $\Delta T_p$ of similar component BMGs [18] and higher than

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**Table 1 Polarization data for Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$, Zr$_{60}$Fe$_{10}$Cu$_{20}$Al$_{10}$, 316L stainless steel and Ti-6Al-4V alloy**

| Alloy                  | $E_{corr}$ (V) | $I_{corr}$ (A) |
|------------------------|----------------|----------------|
| 316L                   | −0.14          | 1.61x10$^{-7}$ |
| Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ (5 mm) | −0.26          | 2.03x10$^{-8}$ |
| Zr$_{60}$Fe$_{10}$Cu$_{20}$Al$_{10}$ (1 mm) | −0.37          | 9.71x10$^{-8}$ |
| Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ (6 mm) | −0.34          | 5.36x10$^{-7}$ |
| Zr$_{60}$Fe$_{10}$Cu$_{20}$Al$_{10}$ (3 mm) | −0.36          | 6.56x10$^{-7}$ |

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Figure 3 DSC curves of Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ BMG with different heating rates
that of Cu–Zr–Al system BMGs [19], suggesting that the specified metallic glass system has a relatively high thermal stability.

The activation energies can be calculated by Kissinger equation as shown below [20]:

\[
\ln \left( \frac{T^2}{\theta} \right) = \frac{E}{RT} + \text{constant},
\]

where \( T \) is the transition temperature (\( T_g \), \( T_x \) and \( T_p \)) under a given heating rate \( \theta \), \( E \) is the activation energy and \( R \) is the gas constant. The activation energy is determined by the slope and standard error of the linear fitted lines from the plot of \( \ln \left( \frac{T^2}{\theta} \right) \) vs. \( 1/T \). The values are calculated for the activation energies at glass transition temperature (\( E_g \)), beginning of crystallization (\( E_x \)) and crystallization peak (\( E_p \)) as 301.4 ± 16.5, 256.91 ± 8.6 and 216.15 ± 2.7 kJ/mol, respectively (Figure 4a).

\( E \) can also be calculated by Ozawa equation, which is shown below [21]:

\[
\ln \theta = -1.0561 \frac{E}{RT} + \text{constant},
\]

where \( \theta \) is the heating rate, \( T \) is the specific temperature (\( T_g \), \( T_x \) and \( T_p \)), \( E \) is the activation energy and \( R \) is the gas constant. From the slopes and standard errors of the linear fitted lines (a plot of \( \ln \theta \) against \( 1/T \)), the activation energies were estimated as 285.90 ± 13.5, 256.07 ± 3.9, 217.74 ± 2.0 kJ/mol for \( T_g \), \( T_x \), \( T_p \), respectively (Figure 4b).

Kissinger and Ozawa methods are the most commonly used ways of calculating non-isothermal kinetic like crystallization activation energy \( E \) or Avrami exponent \( n \). As expected, the activation energies obtained by the two methods are close thereby indicating a good coherence.

Generally, \( E_g \) represents the energy barrier of the structural transformation from the glassy structure to super-cooled liquid region, while \( E_x \) gives information about the difficulty for the transition from the super-cooled liquid to the crystalline phase [22]. From Table 3, the \( E_g \) value is higher than the \( E_x \), which means that the energy barrier for glass transition is higher than that at starting point of crystallization. The thermal stability of BMGs can be evaluated by comparing the activation energies, namely the higher the activation energy, the harder the crystallization proceeds.

Compared with our previous work on Zr60Cu20Fe10Al10 BMG, the \( E_g \) and \( E_x \) of Zr63Fe2.5Cu23Al11.5 BMG are higher than those of Zr60Cu20Fe10Al10, which indicates the Zr63Fe2.5Cu23Al11.5 BMG has a better thermal stability than Zr60Cu20Fe10Al10.

**Table 2** Characteristic temperatures of Zr63Fe2.5Cu23Al11.5 BMG with different heating rates

| Heating rate (K/min) | \( T_g \) ± 1 (K) | \( T_x \) ± 1 (K) | \( T_p \) ± 1 (K) | \( \Delta T_p \) ± 1 (K) |
|----------------------|-----------------|-----------------|-----------------|---------------------|
| 10                   | 652             | 728740          | 750             | 76                  |
| 20                   | 661             | 740752          | 764             | 79                  |
| 40                   | 666             | 752761          | 779             | 86                  |
| 80                   | 677             | 763775          | 795             | 86                  |

**Table 3** The activation energy values (\( E_g \), \( E_x \), \( E_p \)) of Zr63Fe2.5Cu23Al11.5 and Zr60Cu20Fe10Al10 BMGs calculated by Kissinger and Ozawa methods

| BMG Composition          | \( E_g \) (kJ/mol) | \( E_x \) (kJ/mol) | \( E_p \) (kJ/mol) |
|--------------------------|-------------------|-------------------|-------------------|
| Zr63Fe2.5Cu23Al11.5 (Kissinger) | 301.40 ± 16.5     | 256.91 ± 8.6      | 216.15 ± 2.7      |
| Zr63Fe2.5Cu23Al11.5 (Ozawa)  | 285.90 ± 13.5     | 256.07 ± 3.9      | 217.74 ± 2.0      |
| Zr60Cu20Fe10Al10 (Kissinger) | 266.7 ± 21.3      | 240.9 ± 6.4       | 242.3 ± 9.4       |
| Zr60Cu20Fe10Al10 (Ozawa)    | 277.9 ± 21.3      | 241.2 ± 6.0       | 242.7 ± 8.7       |
3.4 Non-isothermal Crystallization Kinetics of Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ BMG

3.4.1 Local Activation Energy (LAE)

Examining the crystallization peaks in the DSC curves obtained under different heating rates (Figure 5a) shows that the range of the crystallization peaks became larger as the heating rate increased. Figure 5a displays a partial DSC curve of Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ BMG at different heating rates. The crystal volume fraction $x$ at any temperature is $x = St/S$, where $S$ is the total area of the crystallization peak between the temperature at which crystallization starts and the temperature at which crystallization is ended, and $St$ is the portion of the crystallization peak up to the temperature $T$ area. Thus, Figure 5b shows the volume fraction of crystallization ($x$) at different temperatures, which is a typical S-shape and consistent with other developed amorphous alloys [23, 24].

Since the local activation energy (LAE) changes in different stages of crystallization procedure [25], the change in LAE with the crystallization volume fraction can be determined. Figure 6a plots the linear fitted relationship between $\ln(\theta)$ and $1000/T$ with different crystallization volume fractions ($x$) from non to all, where the evolution of the LAE calculated by the Ozawa method was expressed in Figure 6b.

$E_c(x)$ shows a downward trend with the increase of $x$, indicating that the energy barrier reduces during the crystallization reaction, making it more available for the crystallization proceeds. At the starting stage ($x < 0.1$), the activation energy decreases rapidly as well as the increasing of $x$, indicating that the process is dominated by nucleation, and the nucleation needs to overcome the high energy barrier. As the crystallization proceeds ($0.1 < x < 0.9$), the curve shows a gradual decreasing tendency due to structural relaxation of the amorphous structure around the crystalline phase. In the ending stage, the
activation energy drops sharply, which reveals the crystallization procedure is dominated by growth.

### 3.4.2 Kinetic Parameter-Evolution of Local Avrami Exponent

To figure out the competition between the nucleation and growth, the crystallization of Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ amorphous alloy was determined based on Johnson-Mehl-Avrami-Kolmogorow (JMAK) model:

$$x = 1 - \exp\left(-kt^n\right),$$

where $x$ and $n$ are crystallization volume fraction and Avrami exponent [26], $k$ is the rate constant related to temperature:

$$k = A \exp\left(-\frac{E}{RT}\right),$$

where $A$ and $E$ are the pre-exponential term and activation energy, $T$ represents the temperature, $R$ is the gas constant and.

Figure 7a shows the JMAK plots of the data measured under various heating rates. As $n$ is variable along the entire crystallization procedure, the local Avrami exponent is employed to represent the corresponding dynamic characteristics as the equation below:

$$n(x) = -\frac{R}{Ec} \frac{\partial \ln \left[-\ln \left(1-x\right)\right]}{\partial \left(\frac{1}{T}\right)}.$$ (5)

The JMAK equation is often employed to describe the isothermal crystallization behavior of BMGs originally, then it is extended to non-isothermal applications [27]. Therefore, in order to measure the Avrami exponent, first we need to plot $\ln\left[-\ln\left(1-x\right)\right]$ versus $1/T$ as shown in Figure 7a. To understand the crystallization behavior of Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ BMG, diffusion-controlled growth theory is often applied. According to this theory, the definition of Avrami exponent is used to determine the variation of nucleation and growth during crystallization procedure [28]. Considering the crystallization in the super-cooled liquid is diffusion-controlled, the Avrami exponent can be divided into the followings [29]: $n < 1.5$ denotes the growth of crystals with an appreciable initial volume; $n = 1.5$ indicates the growth dominates the crystallization procedure with no nucleation occurs; $1.5 < n < 2.5$ indicates the growth governs the crystallization procedure with a lower growth rate and a decreasing nucleation rate; $n = 2.5$ reflects growth of crystals with a constant nucleation rate and $n > 2.5$ indicates the growth of small crystals with an increasing nucleation rate.

Figure 7b reveals the evolution of $n(x)$ depending on $x$ under different heating rates of 10, 20, 40, 80 K/min. $n(x)$ tends to decrease gradually, while the crystallization volume fraction increases. The variation of nucleation and growth rates during crystallization can be speculated by the variation of local Avrami exponent. In particular, the LAEX reduced from 12 to 0.8 under the heating rate of 80 K/min. From Figure 7b it can be seen that if $x < 0.9$ and $n(x) > 2.5$, which refers the generating of nuclei although most of the matrix of Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ BMG has been crystallized, and the nucleation rate increase rapidly from $0 < x < 0.1$ and became smooth from $0.1 < x < 0.9$. When $0.9 < x < 0.98$ and $1.5 < n(x) < 2.5$, indicated that the rate of nucleation is reducing and growth rate increased. When $x > 0.98$, the nucleation procedure tended to end. It can be inferred that the crystallization of Zr$_{63}$Fe$_{2.5}$Cu$_{23}$Al$_{11.5}$ BMG is mainly dominated by nucleation with a decreasing nucleation rate during most of crystallization procedure within $0 < x < 0.9$, after that growth took control and filled the rest of the amorphous matrix.
4 Conclusions
In this work, a high glass forming ability Zr-based BMG with the composition of Zr_{63}Fe_{2.5}Cu_{23}Al_{11.5} was fabricated. The BMG has excellent corrosion resistance, with the corrosion rate of $2.03 \times 10^{-8}$ A/cm$^2$ in a 3.5 wt% sodium chloride solution.

The overall crystallization activation energies of Zr_{63}Fe_{2.5}Cu_{23}Al_{11.5} BMG, calculated by Kissinger and Ozawa methods, were $256.91 \pm 8.6$ and $256.07 \pm 3.9$ kJ/mol, respectively, which denotes that the specified metallic glass system has a relatively high thermal stability.

Then the crystallization mechanism was investigated by JMAK method. The results suggest that the crystallization procedure is mainly dominated by nucleation with decreasing nucleation rate.

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Authors' Contributions
YL & YJ did the corrosion tests, data analysis, writing, they contributed equally. XW and HK prepared the materials, PZ did the DSC & XRD tests. PCZ revised the manuscript. All authors read and approved the final manuscript.

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Competing Interests
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