In-situ structural identification of Zr$_3$Al$_2$ type metastable phase during crystallization of a Zr-based MG

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Abstract:

A metastable phase was detected using higher energy synchrotron radiation when Zr-based metallic glass (MG) was annealed under vacuum in Linkam hot stage at 848 K. The formation and transformation processes of metastable phase were recorded by synchrotron radiation method. The metastable phase during crystallization was identified as Zr$_3$Al$_2$ structure type according to powder diffraction and TEM analysis. The structure of Zr$_3$Al$_2$ type MCP was experimentally evidenced by 3D diffraction patterns and mathematically described. The identification of Zr$_3$Al$_2$ MCP could be helpful for the understanding of cluster structure of MG.

Key Words: metallic glass, metastable phase, crystallization, synchrotron radiation

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1 Introduction

Metallic glasses (MGs) have drawn great attention because of their unique liquid-like structure and the combination of superior properties, including high yield strength, good elasticity, good magnetic properties, high wear resistance and high corrosion resistance [1-3]. Upon heating, MGs undergo a series of thermal events including glass transition temperature ($T_g$), supercooled liquid region ($\Delta T_x$) and crystallization temperature ($T_x$). In several MG systems, it has been reported previously that the crystallization process leads to the formation of distinctive metastable structures, such as metastable crystalline phase (MCP) and metastable quasicrystal phase (MQC), as a result of nucleation of crystals from the non-equilibrium amorphous matrix [4-7]. Previous findings revealed the formation of MCP in Zr$_{55}$Al$_{10}$Ni$_{10}$Cu$_{30}$ MG [6] and MQCs in Zr$_{63}$Cu$_{23}$Al$_{12}$, Zr$_{63}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$ and Zr$_{69.5}$Cu$_{12}$Ni$_{11}$Al$_{7.5}$ alloys during heating [8]. Subsequently, a number of studies were reported that MCPs or icosahedral MQCs were formed in different Zr-based MGs. For example, MQCs were found in Zr-based binary, ternary and multicomponent metallic glass formers with the addition of Ti, Pd or Pt [9-11]. Using fast quenching or ion irradiation methods [12, 13], MCPs or MQCs were also observed in metallic glassy matrix. When 1 wt.% La$_2$O$_3$ was introduced into Zr$_{55}$Al$_{10}$Ni$_{10}$Cu$_{30}$ alloy, MCP and MQC coexisted after thermal treatment [14]. Recent publications concerning metastable and quasicrystal phases formed in Zr-based glassy matrix are listed in table 1, which summarizes compositions or composition range of MCP/MQC formers, formation methods and the structure type of metastable phases.

In addition to alloy composition factor, oxygen impurity in the alloy, which can be introduced from raw materials or annealing environment, were also found to affect the nucleation process of
metastable phases in Zr-based alloys [30, 34]. When the content of oxygen reached 4.3 atomic percent (at.%) in Zr65Cu27.5Al7.5 ternary alloy, MQC had precipitated from glassy matrix [30]. However, when the content was lower than the critical value, another stable crystalline phase instead of MQC appeared. Similar experimental results were demonstrated in another study that high content of oxygen promoted the crystallization of metastable phase via the redistribution of oxygen [34]. Due to the different fabrication environment of MGs, the precipitation of MQCs in Zr65Cu17.5Ni10Al7.5 and Zr69.5Cu12Ni11Al7.5 MGs indicating low reproducible reliability which also can be interpreted by the different contents of oxygen. More recent researches interpreted the crystallization mechanisms in the point of view of thermodynamics and kinetics [37, 38].

In terms of MCP formation in MGs, the same one was found to have nucleated from the glassy matrix in annealed Zr35Al10Ni5Cu30, Zr55Cu20Al10Ni10Pd5 and some other Zr-based MGs according to previous studies [15, 16]. The accurate identification of MCP structure is important because that it could be a strong evidence to interpret the configuration of clusters of metallic glasses. In order to clarify the structure of metastable crystalline phase of Zr-based MGs during crystallization, Zr69.5Cu12Ni11Al7.5 MG was adopted in our work for further investigation. In this work, using high energy synchrotron radiation in transmission mode during in-situ heating and transmission electron microscopy (TEM), the structure of MCP nucleated in Zr69.5Cu12Ni11Al7.5 metallic glass was identified and high temperature crystallization results were investigated.

2 Experimental

Master ingots of Zr69.5Cu12Ni11Al7.5 (at.%) alloy were prepared by arc melting using high purity
metals, which were melted more than 3 times for homogeneity under the protection of high purity argon. Glassy ribbons were synthesized by melt spinning method. The ribbons were annealed under vacuum in a thermal treatment furnace at 848 K and 1073 K, respectively.

The as-spun ribbons without annealing were sealed under protection of argon flow in quartz capillaries and placed on a computer-controlled Linkam hot stage. The temperature was well controlled below the melting temperature of Zr-based alloy to prevent the reaction between Zr and Si of quartz crucible. The in-situ heating samples were examined using high energy synchrotron radiation in transmission on the ID11 beam line of the European Synchrotron Radiation Facilities (ESRF), which was monochromatized using a nitrogen-cooled double crystal silicon monochromater. The photon energy was 80 keV corresponding to an X-ray wave-length ($\lambda$) of about 0.015498 nm. The diffraction spectra were acquired in transmission mode through the quartz capillary in the Linkam by a 2D CCD camera. The heating rate of the Linkam was 10 K/min. Acquisition and data processing times were configured as 20 seconds such that a full spectrum can be obtained.

The annealed samples were ground into the metallic powder. The powder was loaded into a thin glass capillary and mounted in a sample holder on the ID 31 high resolution powder diffractometer with the wave-length ($\lambda$) of 0.050002 nm. The structure of the sample annealed at 848 K was investigated by TEM using selected area electron diffraction (SAED) with the wave-length ($\lambda$) of 0.1542 nm.

3 Results and discussion

The X-ray diffraction patterns obtained under in-situ heating using synchrotron radiation in
transmission mode, the transition in detail from a metastable phase to stable ones, and the volume fractions of different nucleated crystalline phases as a function of temperature are shown in Fig. 1. In Fig. 1 a, Zr60.5Cu12Ni11Al7.5 alloy exhibit fully amorphous microstructure evidenced by the absence of sharp Bragg peaks corresponding to crystalline structures, until the temperature reached $T_x$ (~763 K). The phase initially nucleated from the amorphous alloy can be identified as a metastable phase. When the temperature went higher than 950 K, the peaks of the metastable crystalline phase was disappeared in Fig. 1 a. The phase transition from the metastable phase to stable ones can be clearly observed from Fig. 1 b, which is an enlarged view of Fig. 1 a. The diffraction peaks of disappearing metastable phase and emerging stable ones are marked in Fig. 1 b. The intensity of metastable phase was decreasing with the increase of temperature and the peaks disappear when the temperature reaches about 978 K. From Fig.1a and Fig.1.1b, it appears that the strongest peak of the metastable phase has not vanished completely. However, the peak is shared by the bcc Zr phase, as are many similar peaks in the diffraction pattern.

The stable phases transform from metastable and the new crystalline particles significantly grow in the temperature region of that of diminishing of metastable phase. The volume of each crystalline phase was normalized using the following formula:

$$V_i = \frac{p_{\text{frac}_i}V_{uc_i}}{\sum_{i=1}^{N} p_{\text{frac}_i}V_{uc_i}}$$

(1)

where $p_{\text{frac}_i}V_{uc_i}$ is the phase fraction of phase $i$ and $V_{uc_i}$ is the volume of the unit cell of that phase. In Fig. 1 c, the metastable phase (marked with solid triangle) nucleated at ~790 K, followed by bcc Zr (marked with cross). The volume fraction of MCP decreased from ~0.42 to 0 when the temperature went up from ~890 K to ~990 K. The stable phases including Zr6NiAl3)
(marked by solid square) and Zr\textsubscript{2}Cu (marked with solid diamond) nucleated at about 850 K and 875 K, respectively.

Fig. 2 presents the diffraction pattern of annealed sample at 848 K (marked with black solid squares) using high energy powder X-ray diffractometer. In order to identify the structures of the crystalline phases, a thorough search of a database known as the Pauling Files \cite{39} was made. The structures of all known binary combinations of the four elements zirconium, copper, nickel and aluminum were saved. The program “Powdercell” \cite{40} was used to display the calculated diffraction patterns of these binaries. These are superimposed on top of the diffraction pattern from ID31. The calculated Zr\textsubscript{3}Al\textsubscript{2} and bcc Zr crystalline phase diffraction patterns match very well with the observed pattern of annealed Zr\textsubscript{69.5}Cu\textsubscript{12}Ni\textsubscript{11}Al\textsubscript{7.5} alloy. A Zr\textsubscript{3}Al\textsubscript{2} type structure can be identified for the metastable crystalline phase as marked with solid triangle. In the meantime, bcc Zr can also be observed with very similar diffraction peak positions to those of Zr\textsubscript{3}Al\textsubscript{2}.

When the temperature increased, the transformation from Zr\textsubscript{3}Al\textsubscript{2} MCP to stable phases occurred, as shown in Fig. 1. The crystalline phases annealed at 1073 K were identified using powder diffraction in ID31. The experimental diffraction patterns and the ones form database were compared in Fig 3. The annealed alloy is composed of multi-crystalline stable phases, which include bcc Zr, Zr\textsubscript{2}Cu and ternary intermetallic Zr\textsubscript{6}NiAl\textsubscript{2}. In contrast, there is a complete absence of Zr\textsubscript{3}Al\textsubscript{2} structure type metastable phase in the XRD diffraction pattern. From Fig.1, Fig. 2 and Fig. 3, the whole crystallization process and products are summarized in following equation:

\[
\text{Amorphous Phase} \rightarrow^{1080 K} \text{Zr}_2\text{Al}_2 \text{ MCP} + \text{bcc Zr} + \text{remaining Amor} \rightarrow^{880 K} \text{Zr}_2\text{Cu} + \text{Zr}_6\text{NiAl}_2 \rightarrow^{910 K} \text{bcc Zr} + \text{Zr}_2\text{Cu} + \text{Zr}_6\text{NiAl}_2
\]

The Zr\textsubscript{3}Al\textsubscript{2} structure type metastable phase exhibits good thermal stability, which was observed in Zr\textsubscript{55}Al\textsubscript{10}Ni\textsubscript{5}Cu\textsubscript{30} and Zr\textsubscript{55}Cu\textsubscript{20}Al\textsubscript{10}Ni\textsubscript{10}Pd\textsubscript{5} annealed alloys \cite{15, 18}. The ratio of
transformation temperature over melting temperature is about 0.913. From previous results [15], the annealing temperature of Zr₃Al₂ metastable phase is identified at nearly up to the melting point under fast heating rate. The difference in thermal stability of MCPs could be affected by heating rates and impurities. When the oxygen content goes up to 0.43 at.% [30], the formation of icosahedral quasicrystal phase nucleates instead of Zr₃Al₂ structure type MCP. The variability of MCP and MQC can be interpreted by the affinity of Zr and O and when oxygen concentration reaches critical value. The formation of MCP and MQC was also found to be accompanied by the redistribution of oxygen [30, 34].

Using TEM and selected area electron diffraction (SAED), the structure of Zr₃Al₂ structure type MCP was confirmed. Fig. 4 shows SAED patterns corresponding to three different crystallographic zone axes. The MCP is a tetragonal structured crystal with lattice parameters $a = 7.88(\pm 0.08) \, \text{Å}$ and $c = 7.10(\pm 0.08) \, \text{Å}$. To visualize the crystal structure, the 3D crystal structure image was built and demonstrated in Fig. 5 using “Diamond” method [41]. The structure model is composed of large blue balls and small white ones, representing Zr/Ni/Cu and Al/Ni/Cu atoms, respectively. This means that Ni and Cu are capable of potentially occupying both ball positions. However, taking into consideration that the atomic percentage of Zr in Zr₆₉.₅Cu₁₂Ni₁₁Al₇.₅ alloy and Zr₃Al₂ MCP, and the atomic radii differences between Zr and M (Ni, Cu and Al), it is more probable that Zr atoms reside at the positions of blue balls and M (Ni, Cu and Al) occupy the positions of white balls. Therefore, Zr₃(Ni/Cu/Al)₂ structure may be a reasonable structure of the metastable phase. As an intermediate stage between amorphous and Zr₂M (Zr₂Cu and Zr₆NiAl₂) type stable phases, study on the Zr₃Al₂ structure MCP with good thermal stability may benefit the understanding on the structure of multi-component Zr-based metallic glasses and their
devirtification behaviors.

In summary, the in-situ crystallization processes and the formation of metastable phase in Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5} metallic glass with low content of oxygen were observed and analyzed using high energy synchrotron radiation. The metastable phase during crystallization was found and the structure of MCP was identified as Zr_{3}Al_{2} structure type according to powder diffraction and TEM analysis. The transition from Zr_{3}Al_{2} type MCP to Zr_{2}Cu and Zr_{6}NiAl_{2} was experimentally evidenced by 3D diffraction patterns and mathematically described using volume fraction function.

Acknowledgement

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References


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### Table 1

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Metastable phase</th>
<th>Method</th>
<th>References</th>
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<td>MCP</td>
<td>annealing; ion irradiation</td>
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<td>annealing</td>
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<td>Zr$<em>{70}$Ni$</em>{10}$xPd$<em>{x}$, Zr$</em>{70}$Cu$<em>{30}$xPd$</em>{x}$</td>
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<td>annealing</td>
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<td>MQC</td>
<td>annealing</td>
<td>15, 16</td>
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<td>Zr$<em>{63.3}$Ti$</em>{18.88}$Cu$<em>{15.45}$Ni$</em>{12.33}$</td>
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<td>annealing</td>
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<td>annealing</td>
<td>19, 21</td>
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<td>Zr$<em>{70}$Cu$</em>{20}$Ir$<em>{10}$, Zr$</em>{70}$Cu$<em>{20}$Rh$</em>{10}$</td>
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<td>Zr$<em>{55}$Ti$</em>{0.186}$Nb$<em>{0.058}$Cu$</em>{0.324}$Ni$<em>{0.28}$Al$</em>{0.174}$Al$_{100-y}$ ($y=57$ and 62)</td>
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<td>Composition</td>
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<td>Zr_{55.4}Cu_{27.5}Al_{17.5}O_{x} (x=0.43% and 0.82%)</td>
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<tr>
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<td>MCP (orthorhombic)</td>
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<td>Zr_{70}Ni_{23}Ti_{7}</td>
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<td>33</td>
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<td>(Zr_{65}Al_{7.5}Cu_{27.5})<em>{100-x}Ti</em>{x} (x=2-15 at.%)</td>
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<td>MCP+MQC</td>
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<td>36</td>
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List of figures

Fig. 1 X-ray diffraction patterns using in-situ heating synchrotron radiation (a), the enlarged view showing details of metastable phase transition (b), and volume fractions of crystalline phases in Zr$_{69.5}$Cu$_{12}$Ni$_{11}$Al$_{7.5}$ during heating (c).

Fig. 2 XRD pattern (marked with solid square) of annealed Zr$_{69.5}$Cu$_{12}$Ni$_{11}$Al$_{7.5}$ MG at 848 K using powder diffraction: the metastable phase is identified as Zr$_3$Al$_2$ structure type since the Bragg peaks matched well with the calculated diffraction pattern of Zr$_3$Al$_2$ (solid triangle); bcc Zr (solid ball) was found in annealed sample.

Fig. 3 XRD pattern of Zr$_{69.5}$Cu$_{12}$Ni$_{11}$Al$_{7.5}$ MG annealed at 1073 K. The stable crystalline phases are identified as bcc Zr, Zr$_2$Cu and Zr$_6$NiAl$_2$.

Fig. 4 SAED patterns of Zr$_3$Al$_2$ structure type metastable phase.

Fig. 5 Crystal structure of Zr$_3$Al$_2$ structure type MCP, image created using “Diamond”.
Peaks from higher temperature stable phases emerging

Peaks from metastable phase disappearing

Intensity (a. u.)

2 Theta (deg.)

Temperature (K)

878

913

948

978

1013