The Crystallization Process of Zr-Based Metallic Glass by the Influence of Heating Rate and Alloy Composition

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Abstract. A study of the crystallization process of Zr-based Metallic Glass by the influence of the heating rate and variation of alloy composition was investigated. The alloys used were Zr₆₈Cu₁₄Ni₁₁Al₇, Zr₆₄Cu₁₇Ni₁₁Al₇.₅, and Zr₆₉.₅Cu₁₂Ni₁₁Al₇.₅. Thermal stability was analyzed using DSC (Differential Scanning Calorimetry) with a heating rate of 5°C/min and 10°C/min until the temperature reached 500°C. The three samples were heated with temperature variations of 400°C, 425°C, and 450°C for one hour in air. Crystal growth was observed by XRD test. The DSC curve of the three samples shows that the higher the rate of heating, the shift of the crystallization peak temperature shifts to a higher temperature. At higher temperatures, the crystallization process occurs faster than at lower temperatures. The composition of zirconium contributes to the resistance properties of crystallization. The alloy with the highest zirconium composition has a high resistance to crystallization. The crystalline phase formed is ZrO₂ tetragonal in all samples heated at a temperature of 450°C, and there is an intermetallic phase of Zr₂Ni identified on Zr₆₄.₅Cu₁₇Ni₁₁Al₇.₅

1. Introduction
These guidelines, Metallic glass alloys are metal alloys that have an amorphous structure, and in recent years, research related to metallic glass still receives significant attention [1], [2], [3], [4], [5]. Its amorphous structure makes metallic glass have excellent properties, including oxidation resistance, corrosion resistance, ductility, toughness [6],[7]. Related to usage, besides having superior mechanical strength, the stability of the amorphous structure is also an important concern.

Meanwhile, the structure will change if the amorphous alloy undergoes heat treatment and is in an environment that does not vacuum. Oxygen has a very significant role and maintains an amorphous structure. The amorphous structure will be damaged and transformed into crystals when the amorphous alloy is heat treated at the crystallization temperature and in a high oxygen-containing environment [8], [9], [10]. Structural resistance and resistance to the environment can be identified through structures formed after the alloy has experienced heating, for a long time and in an environment that does not vacuum. Koster has reported that crystallization and oxidation are two phenomena that compete with each other when amorphous alloys are subjected to heat treatment, held for a certain period and not vacuum conditions [11,12], [13].

In this paper, the effect of heating rate and composition on the amorphous structure of Zr-based metal has been studied. Also, it also examines the effect of sample storage time on structural stability.
and oxidation resistance, when the alloy is heated around the crystallization temperature in the air for 1 hour.

2. Experimental Methods
Zr-based amorphous alloys with variations in composition derived from arcs melting Zr, Cu, Ni and Al (> 99.9%) made by melting spinning as reported elsewhere in detail [12,13]. Amorphous alloys have been stored in boxes made of cardboard for more than 20 years. Thermal characteristics of the sample were tested by DSC (Differential Scanning Calorimetry) Type DSC-60 Schimadzu with the variation of heating rate. Stability of amorphous alloy structure investigated by XRD test. Amorphous alloy transformation kinetics can be seen from the DSC curve. And the phase formed in the amorphous alloy during heating around the crystallization temperature was studied from the XRD results.

3. Result and Discussion
Fig. 1 shows the X-ray diffraction patterns for the initial condition of the amorphous Zr-based alloys before heat treatment. In general, all samples are amorphous, even though there is an unidentified small peak in 2θ = 26.48° for Zr64.5Cu17Ni11Al7.5 sample.

The resulted DSC measurement during thermal characterization with different heating rate is shown in Fig 2. Each curve in Fig. 2 expresses the heat flow to the samples that the energy released by the sample to transform into an order of atomic arrangement. On the DSC curve, there does not appear to be a noticeable change in the curve of the baseline, as observed (see insert on Fig.2) by Inoue A. et.al [14]. It indicates that the glass transition temperature does not observe. The initial condition of the sample is not completely amorphous (see Fig.1). Sample storage for a long time does not guarantee that it does not react with oxygen, even if only on the surface. In this alloy, Zirconium has the largest composition, which has a relatively high affinity for oxygen, so oxidation is easy. The oxide formed causes unclear glass transition regions. This one of the reasons for the glass transition on the DSC curve is not obvious. The complete data analysis was shown in Tab. 1.

| No | Samples       | Heating rate (°C/min.) | Crystallization (°C) |
|----|---------------|------------------------|----------------------|
|    |               |                        | Start | Peak | end  |
| 1  | Zr68Cu14Ni11Al7  | 5                      | 393.07 | 419.11 | 425.74 |
|    |                | 10                     | 404.42 | 427.53 | 435.04 |
| 2  | Zr64.5Cu17Ni11Al7.5 | 5                    | 402.24 | 416.87 | 422.96 |
|    |                | 10                     | 418.03 | 426.20 | 431.84 |
| 3  | Zr69.5Cu12Ni11Al7.5 | 5                    | 422.96 | 433.60 | 437.63 |
|    |                | 10                     | 436.92 | 442.26 | 446.51 |
Crystallization temperatures were observed for the heating rate of 5°C/min at the peak of the DSC curve for Zr$_{64.5}$Cu$_{17}$Ni$_{11}$Al$_{7.5}$, Zr$_{68}$Cu$_{14}$Ni$_{11}$Al$_{7}$, and Zr$_{69.5}$Cu$_{12}$Ni$_{11}$Al$_{7.5}$ of 416, 419 and 433°C, while for the heating rate of 10°C/min of 426, 427 and 442°C, respectively. From this data, amorphous Zr-based alloys were then heat treated with the temperature around the crystallization temperature, namely: 400, 425, and 450°C in the air.

**Figure 1.** X-ray diffraction patterns of the initial condition of Zr$_{66.5}$Cu$_{17}$Ni$_{11}$Al$_{7.5}$, Zr$_{68}$Cu$_{14}$Ni$_{11}$Al$_{7}$, and Zr$_{69.5}$Cu$_{12}$Ni$_{11}$Al$_{7.5}$

**Figure 2.** The DSC curves of Zr$_{68}$Cu$_{14}$Ni$_{11}$Al$_{7}$, Zr$_{64.5}$Cu$_{17}$Ni$_{11}$Al$_{7.5}$, and Zr$_{69.5}$Cu$_{12}$Ni$_{11}$Al$_{7.5}$ with different heating rate (a) 5°C/min and (b) 10°C/min.
The DSC curve can also be used to analyze the transformation process. In metallic glass alloys, the kinetics of phase transformation from amorphous to the crystal can be carried out by providing a transformed fraction model. The DSC peak represents the energy released when there is a transformation. Based on the DSC test, data can be described as the transformation kinetic curve model (S curve). The S curve is a plotting of material transformed as a function of time. Fig. 3 shows the transformed fraction curve vs. time for amorphous Zr-based alloys at the different heating rate. From the transformed fraction curve with time shows that the magnitude of the heating rate causes in a curve shift to the right. This is related to the heat transfer or heat flow to the sample. This phenomenon was classified by Wu.

![DSC curve](image)

**Figure 3.** Curve of transformed fraction vs time for (a) Zr_{64.5}Cu_{17.5}Ni_{11}Al_{7.5}, (b) Zr_{68}Cu_{14}Ni_{11}Al_{7} and (c) Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}
In the other side, it has conducted a study related to the effect of heating rate variations on the shift of the DSC curve. It has been reported that the shape of the DSC curve (S curve) is influenced by the heating rate. The peak of the DSC curve will shift to a higher temperature for a higher heating rate. Besides, the rate of crystallization will be faster if the heating rate is relatively high. At a heating rate of 20 - 30°C/min. It produces a more stable crystallization, compared to a heating rate of 5 - 10°C/min. This informs that the increased heating rate causes the crystallization process to occur earlier and in a short time. The S curve in figure 3 - 5 shows that for the crystallization process, up to 80% of the transformed fraction requires a shorter time for the heating rate of 10°C / min than 5°C / min.

Fig. 4 - 6 shows the pattern of the diffraction pattern of Zr-based amorphous alloys composition varies after being heated in the vicinity of the crystallization temperature of 400, 425, and 450°C. At temperatures of 400°C, all samples were still in an amorphous state, except that Zr_{64.5}Cu_{17.5}Ni_{11}Al_{7.5} began to emerge crystalline oxides identified as t-ZrO_2. In general, after being given heat treatment for 1 hour with varying temperatures, the phase formed is, tetragonal ZrO_2 (t-ZrO_2), while phases other than oxide crystals were only identified on Zr_{64.5}Cu_{17.5}Ni_{11}Al_{7.5}. Storage for a long time makes Zr-based metallic glass material, an alloy that has excellent structural stability. There is no phase intermetallic phase like Zr_2Ni when it has been heated for 1 hour.

Meanwhile, it has been reported that the super-Zr-based alloy with the composition Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5} has been crystallized at a temperature of 370°C for 4 hours in the air [5]. The greater the Zr content, the higher the crystallization, which means the stability of the structure is getting better, while at a temperature of 400°C these alloys are still amorphous. Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5} is an alloy that has the best properties for structural stability and oxidation resistance.

**Figure 4.** The XRD patterns of Zr_{68}Cu_{14}Ni_{11}Al_{7} during heating at different temperature for 1 h
4. Conclusion
Storage for a long period of more than 20 years can be identified by the structural stability and oxidation resistance of amorphous Zr-based alloys. The initial oxide layer formed can inhibit its crystallization or can maintain an amorphous structure and oxidation resistance. After heating 400 - 450°C, generally the alloy only undergoes oxidation. The best crystallization and oxidation resistance was found in the Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5} alloy, while the worst oxidation and oxidation resistance was identified on Zr_{64.5}Cu_{17}Ni_{11}Al_{7.5}.

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