OXIDATION BEHAVIOR OF Zr-BASED AMORPHOUS ALLOYS AT 400°- 450°C IN AIR

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ABSTRACT

The study of oxidation behavior of amorphous alloys based on Zirconium with 2 variations in composition was carried out: Zr₆₄.₅Cu₁₇Ni₁₁Al₇.₅ and Zr₆₉.₅Cu₁₂Ni₁₁Al₇.₅ at temperatures of 400-450°C in air. Amorphous Zr-based alloys were thermally characterized using Differential Scanning Calorimeter (DSC) to determine the crystallization temperature and glass transition temperature. The oxidation characterization was carried out using a Thermo gravimetric Analyzer (TGA) at temperatures of 400, 425, and 450°C for 4 hours in air. The phase analysis of the oxidation product was identified using X-Ray Diffraction (XRD). Based on DSC data the crystallization temperature for Zr₆₄.₅Cu₁₇Ni₁₁Al₇.₅ and Zr₆₉.₅Cu₁₂Ni₁₁Al₇.₅ is 426 and 442°C respectively. The oxidation kinetics of the two alloys follows parabolic law and the oxidation rate increases with the addition of temperature. Oxides formed during isothermal oxidation in the Zr₆₄.₅Cu₁₇Ni₁₁Al₇.₅ and Zr₆₉.₅Cu₁₂Ni₁₁Al₇.₅ alloys are t-ZrO₂ (tetragonal) as the dominant phase and ZrO₂ (monoclinic) and CuO as the minor phase. The intermetallic phase is also formed in samples, t-Zr₂Ni and Zr₂Cu.

Keywords: oxidation, amorphous alloy, oxide, intermetallic phase

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Introduction

Research related to Zirconium-based metallic glass material has been carried out. Zirconium as a compound element is used as an reinforcement in steelmaking, porcelain, sports equipment such as golf and racket sticks, and many other applications (Appel, 2000; Mondal, Chatterjee, & Murty, 2007; Telford, 2004). Superior mechanical properties of Zirconium alloys such as high strength, large elasticity limits, good corrosion resistance, low appearance of neutron uptake, resistance to irradiation effects, and other mechanical properties make this material widely studied by researchers (Nikulina, Markelov, & Peregu, 1996; Shin, Jeong, Choi, & Inoue, 2007; W. Zhang, Jia, Zhang, & Inoue, 2007). However, in the high temperature the superior properties of Zirconium based metallic glass will be degraded namely amorphous structure stability and oxidation resistance (Köster & Jastrow, 2007; Neogy et al., 2004; Triwikantoro, Toma, Meuris, & Köster, 1999; Zander & Köster, 2004).

The oxidation resistance of an alloy can be seen from the character of the TGA curve, namely the addition or reduction of mass per unit area as a function of time. Zirconium-based amorphous alloy oxidation kinetics follow parabolic law and the oxidation rate increases with increasing temperature (Kai et al., 2009; Mondal et al., 2007; Triwikantoro & Munawaro, 2008; Triwikantoro et al., 1999). Determination of heating temperature depends on the rate of heating used in the DTA-TG equipment to obtain the value of the glass transition temperature \( T_g \) and the crystallization temperature \( T_x \). The increase in \( T_g \) and \( T_x \) due to the increase in the heating rate is also accompanied by an increase in super cooled liquid areas which indicate that \( T_g \) and \( T_x \) for bulk amorphous alloys are an area of a certain range (Inoue, Zhang, Nishiyama, Ohba, & Masumoto, 1994). In isothermal oxidation for zirconium-based amorphous alloys above the crystallization temperature, it is found that the oxidation rate increases when the temperature is raised, whereas on Zirconium-based Nano crystal alloys the higher the temperature, the lower the oxide rate. The structure has a significant effect on the oxidation rate (Destyorini, Rudyardjo, & Triwikantoro, 2015; Kluge & John, 2015; Köster & Jastrow, 2007).

In this paper the results of the study of zirconium-based amorphous alloy oxidation behavior have been reported for more than 20 years. The study focused on the oxidation behavior above the crystallization temperature in the air to determine the oxidation resistance and the stability of the amorphous structure of the alloy. Identification of the phase of the oxide phase formed and the intermetallic phase is used as an indicator that the alloy has been oxidized and crystallized. The formation of the oxide phase indicates that the alloy is not resistant to oxidation, while the formation of crystals shows that the stability of the amorphous structure has been degraded.

Research Method

The amorphous Zr-based alloys with a variation of composition were arc-melted Zr, Cu, Ni and Al (> 99.9%) to produce of pre-alloy, then were fabricated by melt-spinning as described elsewhere in detail (Triwikantoro et al., 1999). These amorphous alloys have been stored on the plastic in a carton box for more than 20 years. The initial conditions of the samples were tested using Differential Scanning Calorimeter (Type DSC-60 Schimadzu) with heating rate 5°/min and 10°/min to know the crystallization
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temperature, then the structure was investigated using XRD. Furthermore, based on thermal character data of DSC the samples were isothermally oxidized with various temperatures 400, 425 and 450°C during 4 hours in air using TGA. Finally, the oxidized Zr-based amorphous alloys were characterized using XRD to reveal the formed phases after isothermal oxidation treatment.

Results and Discussion

Data from DSC observations are shown in Table 1. The T value (onset) in Table 1 shows the beginning of the transformation, while T\textsubscript{x} is the crystallization temperature. The results of thermal characterization using DSC (Differential Scanning Calorimeter) showed that the value of the crystallization transition temperature depends on the heating rate and the alloy composition of the sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating rate (°C/min)</th>
<th>T\textsubscript{onset} (°C)</th>
<th>T\textsubscript{x} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr\textsubscript{64.5}Cu\textsubscript{17}Ni\textsubscript{11}Al\textsubscript{7.5}</td>
<td>5</td>
<td>402.2</td>
<td>416.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>418.0</td>
<td>426.2</td>
</tr>
<tr>
<td>Zr\textsubscript{69.5}Cu\textsubscript{12}Ni\textsubscript{11}Al\textsubscript{7.5}</td>
<td>5</td>
<td>423.0</td>
<td>433.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>436.9</td>
<td>442.3</td>
</tr>
</tbody>
</table>

The highest crystallization temperature was found in the sample Zr\textsubscript{69.5}Cu\textsubscript{12}Ni\textsubscript{11}Al\textsubscript{7.5} which was 442.3°C with a heating rate of 10°/min, while the lowest crystallization temperature was found in the sample Zr\textsubscript{64.5}Cu\textsubscript{17}Ni\textsubscript{11}Al\textsubscript{7.5} which was 416.9°C for a heating rate of 5°C/min. The magnitude of the heating rate causes the crystallization temperature to shift in a larger direction (see Table 1.). In addition, the shift in temporal crystallization is also caused by the large composition of Zirconium elements. The greater the Zirconium composition, the greater the T\textsubscript{x}. In addition, the Cu element also affects the formation of the amorphous phase into the crystalline phase. The addition of copper alloying elements results in an increase in the reconnaissance rate because Cu atoms have the ability to diffuse to form a more stable crystal structure (Triwikantoro & Fajarin, 2009). The heating rate also affects the crystallization temperature value. This is related to the super cooled liquid area that is formed. Increased T\textsubscript{g} and T\textsubscript{x} due to increased heating rates accompanied by increased super cooled liquid areas (Q. C. Zhang, Pang, Li, & Zhang, 2011).

The TGA test results from the alloys Zr\textsubscript{64.5}Cu\textsubscript{17}Ni\textsubscript{11}Al\textsubscript{7.5} and Zr\textsubscript{69.5}Cu\textsubscript{12}Ni\textsubscript{11}Al\textsubscript{7.5} are presented in Figures 1 and 2. The figure shows changes in mass as a function of time at temperatures of 400°C, 425°C, and 450°C for 4 hours in air. An increase in mass occurs when isothermal oxidation is carried out. Zirconium has a Pilling-Bed worth ratio of 1.56, so the formed oxide is compacting not porous.

The formation of this oxide layer occurs because of the diffusion of oxygen ion ions through the compact oxide layer and the diffusion of metal ions towards the oxide/metal boundary plane, also diffusion of metal ion ions through the oxide layer and reacting at the oxide / gas face boundary. The reaction of oxygen ion ions and metal ion ions in these two face limits increases the thickness of the oxide layer (Birks & Meier, 1983).
The oxidation kinetics of the Zr$_{64.5}$Cu$_{17}$Ni$_{11}$Al$_{7.5}$ and Zr$_{69.5}$Cu$_{12}$Ni$_{11}$Al$_{7.5}$ alloys follow parabolic functions and their kinetic constants can be determined by graphing the relationship of changes in mass per unit area ($\Delta m/A$) with time during isothermal oxidation. This law of parabolic oxidation kinetics is also in accordance with observations made by several researchers (Kai et al., 2009; Triwikantoro & Munawaroh, 2008; Triwikantoro et al., 1999) and also one stage parabolic and two stage parabolic kinetics (Cao, Zhang, & Shek, 2013; Chen, 2013; Hu, Cao, & Shek, 2014; M. Zhang, Yao, Wang, & Deng, 2014). The value of the oxidation rate constant ($K_p$) can be seen in Table 2.

**Table 2. Value of the oxidation rate constant**

<table>
<thead>
<tr>
<th></th>
<th>400°C</th>
<th>425°C</th>
<th>450°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr$<em>{64.5}$Cu$</em>{17}$Ni$<em>{11}$Al$</em>{7.5}$</td>
<td>1.3×10$^{-4}$</td>
<td>1.5×10$^{-4}$</td>
<td>2.3×10$^{-4}$</td>
</tr>
<tr>
<td>Zr$<em>{69.5}$Cu$</em>{12}$Ni$<em>{11}$Al$</em>{7.5}$</td>
<td>1.5×10$^{-4}$</td>
<td>1.7×10$^{-4}$</td>
<td>2.4×10$^{-4}$</td>
</tr>
</tbody>
</table>
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The value of the oxidation rate is constant increases with increasing temperature. Increasing the temperature causes the thermal energy received by the Zirconium alloy to increase. This energy is used by alloys to react with oxygen from outside air. At high temperatures, the atmosphere is oxidative and has the potential for oxidation reactions with metal ions (Birks & Meier, 1983).

The phase formation after the isothermal oxidation treatment with TGA can be identified using XRD. Figures 3 and 4 shows that the diffraction pattern of the alloy after oxidation, which can indicate the oxidation product. In Figures 3 and 4 the oxide product is identified, namely t-ZrO$_2$ (tetragonal) as the dominant phase and t-CuO (tetragonal) and m-ZrO$_2$ (monoclinic) as the minor phase. In addition, the intermetallic phase t-Zr$_2$Ni (tetragonal) and t-Zr$_2$Cu (tetragonal) are also identified. The phase t-ZrO$_2$ (tetragonal) is the dominant phase. This is because Zirconium has a low oxidation potential with oxygen, so it is easy to react with oxygen to form oxides. The t-Zirconia phase evaporates the metastable phase. The increase in temperature and the length of the isothermal oxidation phase m-ZrO$_2$ will be formed. In the Zr-O Phase diagram system there are three types of changes, Monoclinic ZrO$_2$ is formed under temperatures of 1000-1200°C, tetragonal ZrO$_2$ is stable at higher temperatures, and cubic ZrO$_2$ is stable above 1500 °C. The formation of t-ZrO$_2$ and m-ZrO$_2$ oxides after isothermal oxidation around T$_g$ and T$_x$ was also observed by several researchers (Chen, 2013; Kai et al., 2009; Kim, Jeong, & Lee, 2008; Köster & Jastrow, 2007; Lim et al., 2014; Triwikantoro et al., 1999), as well as the minor oxide Al$_2$O$_3$ phase (Kai et al., 2009).

In some temperature conditions it is seen that the amorphous phase has slowly begun to disappear with the appearance of the ZrO$_2$ phase in each variation of heating. An increase in temperature will cause an increase in thermal energy received by amorphous material. Increasing thermal energy causes the nucleus to grow by attracting other atoms from the nucleus that have not yet had time to grow to fill the empty space in the lattice that will be formed. With increasing thermal energy received by amorphous material, the crystal growth continues until the final transformation is obtained from amorphous to crystalline.

![Figure 3. Diffraction Patterns of X-rays of Zr$_{64.5}$Cu$_{17}$Ni$_{11}$Al$_{7.5}$ alloy after oxidation variation temperatures](image-url)
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The intermetallic phase formed shows that at temperatures between 400-450°C Zirconium alloy samples are crystallized. This reinforces the DSC curve data that the crystallization temperature of Zirconium-based amorphous alloys occurs at temperatures between 400-450°C, namely 426°C for Zr$_{64.5}$Cu$_{17}$Ni$_{11}$Al$_{7.5}$ and 442°C for Zr$_{69.5}$Cu$_{12}$Ni$_{11}$Al$_{7.5}$.

The formation of CuO oxide products as a minor phase is associated with a small composition of Cu alloys. The CuO phase formation as a minor phase is inseparable from the chemical affinity that Cu has lower than that of Zr in metallic glass alloys. Cu and electron ions move outward and oxygen ions move inward. This reaction occurs in the oxide layer. As long as Cu oxidation diffuses predominantly outward, oxygen into (Wang et al., 2012).

Conclusion

Based on the results of this study it can be concluded that the heating temperature has a significant effect on isothermal oxidation on Zirconium-based amorphous alloys. Zirconium-based amorphous alloy oxidation kinetics follows parabolic law with the oxidation rate increasing with increasing temperature. The phases formed after isothermal oxidations are t-Zr0$_2$ as the dominant phase while m-ZrO$_2$ (monoclinic) and t-CuO as the minor phase and the intermetallic phase t-Zr$_2$Ni and t-Zr$_2$Cu are formed.

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Cao, W. H., Zhang, J. L., & Shek, C. H.
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