Analysis of Composition, Density, and Thermal Properties of U-Zr-Nb Alloy Powder for Nuclear Fuel

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Abstract. Analyses of composition, density and thermal properties of U-Zr-Nb alloy powder had been carried out. The objective of this experiment was to obtain the composition of constituent elements, the density and the thermal properties of U-6Zr-2Nb, U-6Zr-5Nb, U-6Zr-8Nb alloys produced by a hydride-dehydride process. The research began with the manufacturing of U-6Zr-2Nb, U-6Zr-5Nb, U-6Zr-8Nb alloys through a hydride-dehydride process. The U-6Zr-2Nb, U-6Zr-5Nb, U-6Zr-8Nb alloys obtained were analyzed for their elemental compositions, densities, and thermal properties. Analysis of elemental composition was done using Atomic Absorption Spectroscopy (AAS) technique. Density was observed using autopycnometer. Thermal properties were obtained from Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). The results of elemental composition analysis showed that all impurity elements present in the powders were below the limit of the requirements for nuclear fuel, while the uranium content of each alloy powder was below the required value. The densities of U-6Zr-2Nb, U-6Zr-5Nb and U-6Zr-8Nb were 12.9253 g/cm³, 13.0861 g/cm³, and 11.5464 g/cm³ respectively. U-6Zr-5Nb powder has the highest density. In the phase change transition test using DTA, it was found that in U-6Zr-2Nb powder, the phase transformation (of one phase) took place from 639.21 °C to 662.98 °C while in U-6Zr-5Nb powder, a two-phase transformation occurred. Phase change at the first stage ran from 611 °C to 652 °C and in the second stage, it happened from 730 °C to 746 °C. U-6Zr-8Nb powder underwent a two-phase change in which the first stage ran from 615 °C to 652 °C and the second stage ran from 749 °C to 764 °C. From the heat capacity test using DSC, it was found that the highest heat capacity of 0.84 J/g.K was obtained in U-6Zr-5Nb.

Keywords: elemental composition, density, thermal properties, U-Zr-Nb powder

1. Introduction

Reactor fuels can be classified into two types, namely research reactor fuel group and power reactor fuel group. The development of research reactor fuel is aimed at obtaining high density fuels so that the amount of uranium that can be incorporated into the fuel becomes greater per unit volume. If the fuel density is high, the operating time of the fuel inside the reactor becomes longer. U-Zr-Nb alloys are among fuel candidates for a research reactor which currently uses U₃Si₂/Al. The U₃Si₂/Al fuel has a
limitation, that is the density that can be achieved in its fabrication into a fuel element plate (FEP) can only reach 4.8 gU/cm³ [1]. Therefore, researches to develop high density fuels continue to be done. In order for an alloy to qualify as a nuclear fuel, it must meet several requirements with regard to impurities, thermal properties, physical properties, mechanical properties, and neutronics. Also, chemical composition of a metal alloy will affect its chemical, physical, neutronic, and mechanical properties. Therefore, the chemical composition of a metal alloy for a nuclear fuel needs to be known. In addition to chemical composition, physical properties such as density and thermal properties also need to be known. Higher fuel density means more uranium can be inserted into the fuel, and then the fuel can be used longer in the reactor [2]. Similarly, thermal properties of the fuel such as phase change, enthalpy and heat capacity need to be known. Thermal properties of the fuel relate to its heat stability when used in the reactor. The prediction of phase transformation due to temperature change during use as fuel in the reactor is necessary because it will affect the characteristics and the performance of the fuel. Thermal properties are the key to design and optimize temperatures inside the reactor core [3,4]. The objective of this research was to determine the composition of the constituent elements, the density and the thermal properties of U-6Zr-2Nb, U-6Zr-5Nb, U-6Zr-8Nb that were produced from the hydride-dehydride process.

U-Zr based alloys have long been developed as research reactor fuels. Komar Varela et al have developed a U-Zr-Nb alloy with Zr and Nb compositions of 28.2 - 66.7% and 0 - 13.3%, respectively, fabricated using monolithic techniques as in Zircaloys cladding and quenching [5]. In the Komar Varela research, it was found that the U-Zr-Nb alloy with Zr content of 52.1% and Nb content of 9.6% (U-52.1Zr-9.6Nb) produced a mini fuel element plate that contains largest γ-phase uranium. Greater amount of γ-phase uranium in the fuel means greater fuel stability. Rafael Witter Dias Pais et al have also made U-2.5Zr-7.5Nb (Zr = 2.5% and Nb = 7.5%) fuel intended for research, test, advanced high flux, power, and fast reactors [6]. The results of their experiments showed that U-Zr-Nb alloys have high thermal conductivity, ease of fabrication, good compatibility with cladding, and high density. In previous research, Masrukan et al have developed U-6Zr alloy fuel with Al-Mg₂ alloy cladding in the form of mini fuel element plates. The U-6Zr alloy is made from an ingot to powder and characterized to know its mechanical, physical, microstructure properties, and corrosion resistance [7]. The characteristics of U-Zr-based fuels can be improved by addition of metal elements. Some metal elements, such as Ti, Nb, Mo, and Si, can be added to U-Zr alloys. The addition of these metal elements to the U-Zr alloy is to expand the γ-phase region in addition to improving corrosion resistance [5,8,9]. In this research, U-Zr-Nb powder was made through a hydride-dehydride process to produce a brittle U-Zr-Nb ingot so that it can be easily made powder. The powder obtained was analyzed for its elemental composition, density, and thermal properties. It is hoped that the data obtained from these experiments can be used to develop better research reactor fuels.

2. Methodology

U-6Zr-2Nb, U-6Zr-5Nb, and U-6Zr-8Nb alloy powders were made from their ingots. The ingots were made by melting U, Zr and Nb metals in an electric arc furnace operating at a current of 150A and equipped with water cooling. The obtained ingots were cut into pieces and fed into a retort tube on a hydride-dehydride equipment for processing into powder. The cut ingots underwent hydride-dehydride process operated at 350°C while H2 (hydriding) gas was flowed in a vacuum pressure of 10⁻⁶ torr. After the first step of the process was done, the brittle ingots were milled and sieved into fine powder. Thermal properties analysis was done using Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) equipments. Analysis of U-6Zr-2Nb, U-6Zr-5Nb and U-6Zr-8Nb using DTA is intended to know the phase transformation. DSC was used to know the heat capacity.
3. Results And Discussion

3.1. Composition of elements and impurities

Results of the impurity element composition test using AAS technique in Table 1 showed that U-6Zr-2Nb, U-6Zr-5Nb, and U-6Zr-8Nb alloy samples met the specifications for a research reactor fuel. The amounts of impurity elements were below the limit of the requirements for a nuclear fuel. If the amount of an impurity element is large enough, it can form a new phase when reacting with U, Zr or Nb. Formation of a new phase can affect the fuel performance in the reactor. With regards to elements that have high microscopic neutron absorption cross section, the U-6Zr-2Nb, U-6Zr-5Nb, U-6Zr-8Nb alloys tested did not contain Cd and B. The microscopic neutron absorption cross section of Cd and B are 2520 and 767 barns respectively [10]. Since Cd and B were not found in U-6Zr-2Nb, U-6Zr-5Nb, U-6Zr-8Nb alloys, it can be said that the tested alloys fulfilled the neutronic properties requirements for a nuclear fuel.

| Element | In U-6Zr-2Nb | In U-6Zr-5Nb | In U-6Zr-8Nb | Specification |
|---------|--------------|--------------|--------------|---------------|
| Ag      | Not detected | Not detected | Not detected |               |
| Al      | 243.65 ± 2.69 | 228.37 ± 3.32 | 322.24 ± 1.02 | < 600.00 ppm  |
| Ca      | 48.84 ± 1.86  | 62.64 ± 0.63  | 47.98 ± 0.15  | < 100.00 ppm  |
| Cd      | Not detected  | Not detected  | Not detected  | < 2.00 ppm    |
| Cu      | 38.04 ± 0.45  | 19.08 ± 0.1   | 37.00 ± 0.25  | < 80.00 ppm   |
| Co      | Not detected  | Not detected  | Not detected  | < 10.00 ppm   |
| Cr*     | 28.57 ± 0.65  | 19.14 ± 0     | 22.58 ± 0.341 | < 100 ppm     |
| Fe*     | 175.71 ± 3.43 | 141.92 ± 1.69 | 160.10 ± 3.16 |               |
| Mg      | 8.51 ± 0.35   | 2.83 ± 0      | 9.91 ± 0.6    | < 50.00 ppm   |
| Mn      | 10.69 ± 0.52  | 12.69 ± 0.05  | 6.06 ± 0.071  | < 5.00 ppm    |
| Ni*     | 2.63 ± 0.35   | 18.82 ± 0.25  | 23.00 ± 0.73  | < 150.00 ppm  |
| Si      | 23.66 ± 0.55  | Not detected  | Not detected  |               |
| Mo      | -             | Not detected  | 3.32 ± 0.001  | -             |
| Pb      | -             | 31.21 ± 0.35  | Not detected  | -             |
| Sn      | -             | -             | 14.16 ± 0.45  | -             |
| Zn      | -             | -             | 22.11 ± 0.28  | < 1000.00 ppm |
| B       | Not detected  | Not detected  | Not detected  | < 10.00 ppm   |
| Li      | -             | -             | 0.04 ± 0      | < 10.00 ppm   |
The U content of the alloys is shown in Table 2. The difference between planned and observed values exceeded the limit required for each alloy. In the manufacture of a fuel alloy, the precision of U content is important and needs to be considered because it directly affects fuel performance in the reactor.

**Table 2.** Uranium content in U-Zr-Nb alloys

| Alloy           | Planned | Observed | Difference |
|-----------------|---------|----------|------------|
| U-6Zr-2Nb       | 92      | 89.307   | 2.693      |
| U-6Zr-5Nb       | 89      | 85.568   | 3.432      |
| U-6Zr-8Nb       | 86      | 83.553   | 2.447      |

3.2. Alloy powder density

Results of the density test on the alloys in Table 3 show that the highest density took place in the alloy that contains 5 weight % of Nb (i.e. U-6Zr-5Nb). Table 3 shows the density values of U-6Zr-2Nb, U-6Zr-5Nb and U-6Zr-8Nb alloys. Nb has a lower density than either Zr or U. The densities of U, Zr and Nb are, respectively, 18.7 g/cm³, 6.5 g/cm³, and 8.57 g/cm³ [11]. Intuitively, a greater amount of Nb in a U-Zr-Nb alloy should result in the alloy’s lower density. However, density is also affected by phase transformation. The phases of U-6Zr-2Nb, U-6Zr-5Nb, and U-6Zr-8Nb powders are (β + γ), (β + γ) and γ, (α+ γ) and γ respectively. Therefore, the density values of the alloy powders vary considerably. A nuclear fuel required a high density for U. If the amount of U inserted into the fuel is higher, then the fuel life in the reactor will be longer [3].

**Table 3.** U-Zr-Nb alloy powder density

| Alloy     | Density (g/cm³) |
|-----------|-----------------|
| U-6Zr-2Nb | 12.9253         |
| U-6Zr-5Nb | 13.0861         |
| U-6Zr-8Nb | 11.5464         |

3.3. Thermal properties of U-6Zr-2Nb, U-6Zr-5Nb and U-6Zr-8Nb alloys

The results of thermal properties test using DTA is shown in Figures 1, 2, and 3. Figure 1 shows the phase transformation in U-6Zr-2Nb alloy from (α + δ1 + γ) to (β + γ) that took place at the temperatures between 639.21 °C and 662.98 °C.
Figure 1. Thermogram of U-6Zr-2Nb

Figure 2 which is a thermogram of U-6Zr-5Nb shows a double phase transformation. The first one was from \((\alpha + \delta 1 + \gamma\text{Nb})\) to \((\beta + \gamma)\) that ran from 611°C to 652°C. The second one was a transformation from \((\alpha + \delta 1 + \gamma\text{Nb})\) to \(\gamma\) that ran from 730°C to 746°C.

Figure 2. Thermogram of U-6Zr-5Nb

U-6Zr-8Nb alloy also underwent a double phase transformation. The first one was from \((\alpha + \delta 1 + \gamma\text{Nb})\) to \((\dot{\alpha} + \gamma)\) which ran in the temperatures between 615°C and 652°C. The second one was from \((\alpha + \delta 1 + \gamma\text{Nb})\) to \(\gamma\) that ran from a temperature of 749°C to 764°C.

In U-6Zr-2Nb alloy, there was only a single phase transformation, whereas in the other two alloys there were double phase transformations. This is because U-6Zr-2Nb alloy contained powder with a small amount of Nb (2%) that when it was heated at high temperatures, a single phase transformation to \((\beta + \gamma)\) occurred. In the case of U-6Zr-5Nb and U-6Zr-8Nb, each alloy has a greater amount of Nb that when it was heated at high temperatures a double phase transformation to \((\dot{\alpha} + \gamma)\) and \(\gamma\) occurred. All phases formed above are in accordance to the phase diagram of U-Zr-Nb [7].
The result of heat capacity testing using DSC equipment is shown in Figure 4. It can be seen from Figure 4 that the heat capacity values of U-6Zr-2Nb alloy at the temperatures between 35°C and 216°C tended to decrease. Up to a temperature of 216°C, the heat used to increase the powder temperature was relatively low hence smaller heat capacity values. Beyond 216°C until 437°C the heat required to increase the powder temperature was higher hence greater heat capacity values. U-6Zr-5Nb alloy had a similar trend as in the U-6Zr-2Nb alloy. In U-6Zr-5Nb alloy at a temperature range between 35°C and 136°C, the heat capacities decreased from 1.11 to 0.3 J/g.°C. From then up to a temperature of 236°C, heat capacities increased to 0.84 J/g.°C. For U-6Zr-8Nb alloy, it was observable that from a temperature range between 35°C and 75°C, heat capacity values decreased from 1.13 J/g.°K to 0.05 J/g.°K. From then up to a temperature of 437°C, heat capacities increased to 0.27 J/g.°K. The highest heat capacity was observed in the U-6Zr-5Nb alloy that was heated up to 236 °C. It had a value of 0.84 J/g.°K. It was caused by phase transformations in each powder. Phase transformation affected heat capacity on the alloy.

Considering the Nb content in each alloy, it was observed that the higher the Nb content, the decrease in heat capacity values happened at a lower temperature range as shown in Figure 4. For U-6Zr-2Nb, the decrease happened between 35°C and 216°C. For U-6Zr-5Nb, the decrease happened between 35°C and 136°C. For U-6Zr-5Nb, the decrease happened between 35°C and 75°C.
4. Conclusion
From U-6Zr-2Nb, U-6Zr-5Nb, and U-6Zr-8Nb alloys produced, it was observed that the impurities in the alloys were within the limits of nuclear fuel requirements. However, the U contents were below the minimum requirement. U-6Zr-5Nb alloy had the highest density of 13.0861 g/cm³. U-6Zr-2Nb alloy underwent single phase transformation, while both U-6Zr-5Nb and U-6Zr-8Nb alloys experienced double phase transformation. It was also observed that the higher the Nb content in U-6Zr-Nb alloy, the decrease in heat capacity values happened at a lower temperature range. The highest heat capacity was in U-6Zr-5Nb powder with a value of 0.84 J/g°C.

Acknowledgements
The authors would like to acknowledge Mr. Suyoto, Mr. Yatno D.A. Susanto, Mr. Slamet Pribadi, Ms. Asminar, and Ms. Mujinem who have prepared specimens and conducted measurements in this research.

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