NEUTRON DIFFRACTION TECHNIQUE ON THE STRUCTURAL IDENTIFICATION OF ZrNbMoGe ALLOY

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ABSTRACT

The ZrNbMoGe alloy which is extremely hard and brittle has been developed as a candidate for structural materials of cladding for nuclear fuel elements. The melting process is conducted to form a new intermetallic ZrNbMoGe system. Several samples with a varied composition of Ge were successfully synthesized in the preparation. The raw materials; Zr, Nb, Mo, Ge were melted at above 1850°C in argon atmosphere using the arc-melting furnace in PTNBR Bandung. The sample was remelted four times (flapping). The crystal structures were characterized by using the neutron diffraction technique (HRPD) in PTBIN Serpong, to further complement the measured X-ray data. The X-ray diffraction patterns indicated that the new zirconium alloys belong to the hexagonal close packed crystal system with the lattice parameters of $a = 3.23\,\text{Å}$, $b = 3.23\,\text{Å}$ and $c = 5.14\,\text{Å}$, and leading to the hypothesis that precipitates of ZrMo$_2$ and ZrGe are formed in the samples, while they slowly cool down to room temperature. The former sample belongs to the body centered cubic crystal system lattice with lattice parameter of $a = 7.59\,\text{Å}$ and the last sample is an orthorhombic crystal system with the lattice parameters of $a=7.07\,\text{Å}$, $b=3.90\,\text{Å}$ and $c=5.39\,\text{Å}$. The results show that neutron diffraction method is able to distinguish between the ZrMo$_2$ and ZrGe precipitates, and also that the cubic structure of MoGe$_2$ phase appears at the diffraction angle of $2\theta = 44.29^\circ$.

Keywords: Crystal Structure, ZrNbMoGe Alloy, Precipitate.

INTRODUCTION

Diffraction methods (X-ray and neutron) is among widely used instrumental techniques in the various branches of materials science. It is a fast and non destructive technique for identification of compounds and for detection of structural changes produced in a compound by physical and chemical process. The technique is not the most sensitive and quantitative analytical technique [1] available today and it is relatively inexpensive and is consequently available to the majority of problems of solid state.

Centre for Technology and Industrial Nuclear Materials (PTBIN) in BATAN has the type of instruments used in the identification of any crystalline compounds by using neutron diffraction technique; i.e. high resolution powder diffractometer (HRPD). The instrument has 32 high sensitivity detectors which can measure simultaneously the diffraction patterns of a compound. The HRPD is such a powerful non destructive instrument for characterizing
crystal structure of materials. It is evident from the peak to background ratio, which is very sharp.

Because neutrons have a penetration power several orders of magnitude higher than X-rays in most engineering materials, neutron diffraction is the preferred method for the measurement of the bulk crystal structures. This prescribed that the scattered thermal neutrons from reactor beam could be used to deeply analyze the structure of bulky materials by a simple preparation. Therefore a complete set of structure related data will be delivered. Nevertheless many problems also arise from the neutron techniques, lower flux, on the average longer measurement time (sometimes very long), sometimes unpredictable operational schedules coupled with a long waiting list, interrupted operations due to lengthy maintenance period and so on.

Research on the synthesis of zirconium alloys [2], by adding the minor element of Mo, Nb and Ge has been performed in PTBIN BATAN using a single arc-furnace for melting the compounds. It is found that the synthesized alloys have a very high hardness and strength, and are even brittle and difficult to be rolled. In this paper, the application of high-resolution neutron powder diffraction method to identify the crystal structure of the bulk ZrNbMoGe alloy is described. The aim is to verify the experimental X-rays data [3] of ZrNbMoGe alloys, in order to have a good validation of the data. In a previous research Parikin et.al. have used the X-ray diffraction method to measure the crystal structure of the alloys prepared with various mass fraction of Ge element. In this paper the present authors present the comparison of the experimental results from neutron diffraction with the X-ray experimental data.

THEORETICAL

Diffraction is the result of radiation being scattered by regular array of scattering centres whose spacing is about the same as the wavelength of the radiation. For diffraction to occur, Neutron beams scattered off adjacent crystal planes must be in phase. Otherwise, destructive interference of waves occurs and essentially no scattering intensity is observed. At the precise geometry [4,5] for constructive interference (scattered waves in phase), the difference in path length between the adjacent neutron beams is some integer number (n) of radiation wavelengths (λ). The relationship that demonstrates this condition is the Bragg equation:

\[ n\lambda = 2d \sin \theta \]  

where: \( d \) is the spacing between adjacent crystal planes (interplanar spacing) and \( \theta \) is the angle of scattering beams. The \( \theta \) angle is usually referred to as the Bragg angle and the angle \( 2\theta \) is referred to as the diffraction angle because that is the angle measured experimentally.

The magnitude of the interplanar spacing (\( d \)) is a direct function of the Miller indices for the plane and it is depend to the crystal structure system. For a cubic system the relationship is fairly simple. The spacing between adjacent \( hkl \) planes [6] is

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]  

where: \( a \) is the lattice parameter (edge length of the unit cell). For a tetragonal and hexagonal system respectively, the relationship are more complex;

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + \left(\frac{a^2}{c^2}\right)l^2}} \]
Neutron Diffraction Technique On The Structural Identification......

\[
d_{hkl} = \frac{a}{\sqrt{\frac{4}{3}(h^2 + hk + k^2) + \frac{a^2}{c^2}l^2}}
\]

where: \(a\) and \(c\) are the lattice parameters.

EXPERIMENTS

Synthesis of zirconium alloy was carried out by melting the elements of zirconium, niobium, molybdenum and germanium, using single arc melting furnace in the argon atmosphere with the temperature more than 1850°C. The weight percentage of the elements of the ingot being made was 95% Zr, 2.0% Mo, 1.0%Nb and 2.0% Ge. All of these elements were melted into the copper crucible which is equipped by water coolant. By using tungsten electrode, with argon capacity of 5 liters/minute and electric current of 150 Ampere, the elements were burned and melted. After that, the ingots were directly cooled into atmospheric condition to obtain ingots of zirconium alloy. Figure 1 illustrates the experimental steps of the fabrication (a) raw of materials, (b) single arc melting furnace and (c) the ZrNbMoGe ingot. Tabel 1 shows the compositions of the samples, which have been made in the experiment.

![Figure 1](image)

The samples were characterized using a high resolution powder diffractometer (HRPD) in the neutron scattering laboratory (BSN) PTBIN BATAN. The instrument has a wave length of 1.8195 Å, which can penetrate deeply into the materials up to a depth of 4 cm [7]. The neutron diffraction patterns were obtained in the range of \(\theta – 2\theta\) geometry with a very good result in peak to background ratio. Measurements were performed in step of 0.05° in the range of 2\(\theta\) from 2.5° to 150°.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition of the elements (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-pure</td>
<td>Zr: 100, Nb: 0, Mo: 0, Ge: 0.00</td>
</tr>
<tr>
<td>ZrNbMoGe</td>
<td>Zr: 95.00, Nb: 1.0, Mo: 2.00, Ge: 2.00</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Figure 2 shows the diffraction pattern of pure zirconium and its alloy (ZrNbMoGe), obtained by using X-ray diffractometer with a Cu-target (\(\lambda = 1.5405\)Å). The diffraction angle covered is in the range of 20=30° to 20=75°, with a step width of 0.05° in the step-counting scan mode.
The pattern shows sufficiently good peak to background ratio and all peaks are clearly visible. Figure 2a shows that the first three peaks of hexagonal closed packed zirconium appear between the angle of $2\theta = 30^\circ$ and $2\theta = 40^\circ$. Firstly, the peak of $(10\bar{1}0)$ plane is at the angle of $2\theta = 32^\circ$, then, the two highest peaks of zirconium appearing at the angle of $2\theta = 34.90^\circ$ and $2\theta = 36.55^\circ$ correspond to the (0002) and (10$\bar{1}$1) planes respectively.

![X-ray diffractogram of (a) Pure zirconium and (b) ZrNbMoGe alloy](image)

**Figure 2:** X-ray diffractogram of (a) Pure zirconium and (b) ZrNbMoGe alloy [2,3]

Analysis of the diffraction pattern is started from among the three major peaks of zirconium, i.e.: $(10\bar{1}0)$, (0002) and (10$\bar{1}$1) plane. Noticeable in figure 2b are several minor peaks arising in between the first three major peaks of zirconium, i.e.: at the angle of $2\theta = 33.6^\circ$, $2\theta = 34.3^\circ$, $2\theta = 35.5^\circ$ and $2\theta = 37.4^\circ$. These indicate the intermetallic compounds of ZrMo$_2$, ZrGe (210) [8], ZrGe(102) and MoGe$_2$ [9] respectively. Parikin et.al. [3] reported that these peaks are known to belong to precipitates which were formed as the materials cooled down to room temperature.

The X-ray profile seems to agree with the neutron diffraction profile shown in Figure 3. The profile was obtained by the high resolution powder diffractometer (HRPD), with a wavelength of about 1.8195 Å. As in the X-ray profile, several new peaks are also detected in the neutron diffraction profile among the principal peaks (green arrow) of zirconium. These peaks were identified by some vertical colouring arrow; i.e. a yellow one for ZrMo$_2$, an
Neutron Diffraction Technique On The Structural Identification......

orange one for ZrGe and a purple one for MoGe₂. Further identification shows that these minor peaks are belonging to the precipitates that were formed during the cooling process of the alloys [10]. If the experimental setup could be adjusted in such a manner that enable the apparatus to zoom in between the angle of $2\theta=35^\circ$ and $2\theta=47^\circ$, then the minor peaks of the precipitates can be seen more clearly.

![Pattern of ZrNbMoGe alloy](image1)

**Figure 3:** Neutron diffractogram of ZrNbMoGe alloy, taken by using high resolution powder diffractometer at Neutron Scattering Laboratory, PTBIN BATAN.

In Figure 4, the minor peaks appearing in between the first three major peaks of zirconium (green arrows) are clearly visible, i.e.: at the angle of $2\theta=39.70^\circ$, $2\theta=42.49^\circ$ and $2\theta=44.29^\circ$; These peaks can be marked as the reflection plane of ZrMo₂ (220), ZrGe (102) and MoGe₂ (110) respectively. The ZrGe (210) plane does not appear due to the statistical limitation [5] of the neutron scattering data.

![Pattern analysis between the first 3 major peaks of ZrNbMoGe](image2)

**Figure 4:** Analysis of ZrNbMoGe diffraction pattern in between the first 3 major peaks of zirconium alloy.

Both the X-ray and the neutron diffraction profiles, provide information which is no different from each other with respect to the materials’ analysis. Although X-ray can only provide information concerning the surface layer because of its limited penetration capacity, and especially when compared to neutrons which are able to penetrate deeply over several layers into the materials. The result of the $d$-spacing calculations listed in Table 2 show that
the values resulting from X-ray and neutron diffraction are close to the $d$-spacing values given in literature and are listed in the last column of the table. The calculations were performed by using Bragg formula given by equation (1). By using different wavelength of the scattered beams, the position of the reflection peaks ($2\theta$) in the diffraction pattern will shift either to higher or lower values of $2\theta$ angle. The $2\theta$ shifting occurs because of the inherent property of the X-ray wavelength (1.5405 Å) and the neutron wavelength (1.8195 Å) which could shift the diffraction angle to higher $2\theta$ values when the wavelength is longer.

Table 2: The comparison of $d$-spacing calculation on the ZrNbMoGe, obtained from X-ray and neutron diffraction.

<table>
<thead>
<tr>
<th>$2\theta$ deg</th>
<th>Sin $\theta$</th>
<th>$d_{hkl}$ Å</th>
<th>Peak of the plane</th>
<th>$2\theta$ deg</th>
<th>Sin $\theta$</th>
<th>$d_{hkl}$ Å</th>
<th>Peak of the plane</th>
<th>Ref. $d_{hkl}$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray ($\lambda = 1.5405\text{Å}$)</td>
<td>Neutron ($\lambda = 1.8195\text{Å}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.00</td>
<td>0.2757</td>
<td>2.7933</td>
<td>Zr (10i0)</td>
<td>37.85</td>
<td>0.3244</td>
<td>2.8039</td>
<td>Zr (10i0)</td>
<td>2.79</td>
</tr>
<tr>
<td>33.60</td>
<td>0.2891</td>
<td>2.6638</td>
<td>ZrMo$_2$ (220)</td>
<td>39.70</td>
<td>0.3397</td>
<td>2.6782</td>
<td>ZrMo$_2$ (220)</td>
<td>2.68</td>
</tr>
<tr>
<td>34.30</td>
<td>0.2979</td>
<td>2.6111</td>
<td>ZrGe (210)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.62</td>
</tr>
<tr>
<td>34.90</td>
<td>0.2999</td>
<td>2.5676</td>
<td>Zr (0002)</td>
<td>41.30</td>
<td>0.3528</td>
<td>2.5787</td>
<td>Zr (0002)</td>
<td>2.57</td>
</tr>
<tr>
<td>35.50</td>
<td>0.3049</td>
<td>2.5255</td>
<td>ZrGe (102)</td>
<td>42.49</td>
<td>0.3625</td>
<td>2.5097</td>
<td>ZrGe (102)</td>
<td>2.52</td>
</tr>
<tr>
<td>36.55</td>
<td>0.3137</td>
<td>2.4534</td>
<td>Zr (10i1)</td>
<td>43.34</td>
<td>0.3694</td>
<td>2.4628</td>
<td>Zr (10i1)</td>
<td>2.46</td>
</tr>
<tr>
<td>37.40</td>
<td>0.3207</td>
<td>2.4015</td>
<td>MoGe$_2$ (110)</td>
<td>44.29</td>
<td>0.3771</td>
<td>2.4125</td>
<td>MoGe$_2$ (110)</td>
<td>2.41</td>
</tr>
</tbody>
</table>

Figure 5: Phase diagram of binary system Zr-Ge [8]

The formation of precipitates in Zr and Ge intermetallic compounds has been mentioned briefly in the X-ray analysis section. [2,3]. According to the phase diagram [11] shown in Figure 5, four binary compounds can be formed between Zr and Ge: Zr$_3$Ge, Zr$_5$Ge$_3$, ZrGe and ZrGe$_2$. In diffusion pairs of the type Zr-Ge in the temperature range 1023-1153 °K, ZrGe$_2$ is the only reaction layer. Here, neutron scattering technique makes a correction regarding the precipitation formation in a ZrNbMoGe system, where it was verified that ZrGe and not Zr$_3$Ge is the last derivative of the binary compounds of Zr-Ge. Further, it was Rietveld analysis which gives a good fit in the profile refinements, which will be discussed in the next study reports.
CONCLUSION

In summary, it can be concluded that the crystal structure of ZrNbMoGe alloy consists of a pure zirconium i.e. hexagonal closed pack (hcp) with lattice parameters of \(a=3,23\,\text{Å}, \ b=3,23\,\text{Å} \) and \(c=5,14\,\text{Å}\), and the structure of ZrMo2 i.e. body centered cubic (bcc) with lattice parameters of \(a= b= c=7,59\,\text{Å}\), and the structure of ZrGe i.e. orthorhombic with lattice parameters of \(a=7,07\,\text{Å}, b=3,90\,\text{Å} \) and \(c=5,39\,\text{Å}\), and the structure of MoGe2 i.e. tetragonal (bct) with lattice parameters of \(a=b=3,3313\,\text{Å} \) and \(c=8,195\,\text{Å}\). There is no significantly different information between the X-ray and neutron scattering in the crystal structure analysis of the materials.

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