

QUANTITATIVE PHASE ANALYSIS OF THE ZrNbMoGe ALLOYS USING NEUTRON DIFFRACTION TECHNIQUES

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ABSTRACT

QUANTITATIVE PHASE ANALYSIS OF THE ZrNbMoGe ALLOYS USING NEUTRON DIFFRACTION TECHNIQUES. Quantitative analysis by neutron diffraction technique can be utilized to measure not only the type of compounds but also the amount of compounds present in a solid or powder system. The technique has been proven for a composition analysis due to offering some advantages particularly for elements with very similar atomic numbers, and for their high penetrating power. A quantitative phase analysis experiment by using neutron diffraction has recently been carried out to determine the amount present of phases in ZrNbMoGe system. The data analysis was obtained by Rietveld refinement method. The result shows that the profiles have a very good fitting ($R_{wp} = 12.62\%$, 15.45% and 16.39%) with the number of reliable factor among 1.0 and 2.0. The phases of Zr, $ZrMo_2$, Zr_3Ge and ZrGe are identified in the specimens. The ZG1 specimen contains of 94.19 %wt of Zr phase, 2.05 %wt of $ZrMo_2$ phase, 3.15 %wt of Zr_3Ge and 0.59 %wt of ZrGe phase. Whereas the ZG2 specimen comprises of: 84.45 %wt of Zr phase, 4.16 %wt of $ZrMo_2$ phase, 10.18 %wt of Zr_3Ge and 1.20 %wt of ZrGe phase. The volume fraction of the minor phases on specimens shows an increase as addition in Ge content.

Keywords : ZrNbMoGe alloys, Rietveld method, Neutron diffraction

ABSTRAK

ANALISIS KUANTITATIF FASA PADUAN ZrNbMoGe MENGGUNAKAN TEKNIK DIFRAKSI NEUTRON. Analisis kuantitatif dengan teknik difraksi dapat digunakan untuk mengukur tidak hanya tipe senyawa tapi juga sejumlah senyawa yang ada dalam sebuah sistem padatan atau serbuk. Teknik ini telah teruji untuk analisis komposisi bahan karena menawarkan beberapa keuntungan tertentu; khususnya pada unsur-unsur dengan nomor atom berdekatan, dan neutron memiliki daya tembus yang tinggi. Percobaan analisis kuantitatif fasa menggunakan teknik difraksi neutron baru-baru ini telah diterapkan untuk menentukan sejumlah fasa yang ada dalam sistem ZrNbMoGe. Analisis data diperoleh dengan menggunakan metode penghalusan Rietveld. Hasil memperlihatkan bahwa profil penghalusan memiliki parameter fitting yang sangat bagus ($R_{wp} = 12,62\%$, $15,45\%$ dan $16,39\%$) dengan nilai faktor kepercayaan berkisar antara 1,0 dan 2,0. Fasa-fasa Zr, $ZrMo_2$, Zr_3Ge dan ZrGe teridentifikasi dalam spesimen. Spesimen ZG1 mengandung: 94,19 %berat fasa Zr; 2,05 %berat fasa $ZrMo_2$ phase; 3,15 %berat fasa Zr_3Ge dan 0,59 %berat fasa ZrGe. Sementara spesimen ZG₂ mengandung 84,45 %berat fasa Zr; 4,16 %berat fasa $ZrMo_2$; 10,18 %berat fasa Zr_3Ge dan 1,20 %berat fasa ZrGe. Fraksi volume fasa minor dalam spesimen memperlihatkan peningkatan saat kandungan unsur Ge bertambah.

Kata kunci : Paduan ZrNbMoGe, Metode Rietveld, Difraksi neutron

INTRODUCTION

Quantitative phase analysis can be used to measure not only the type of compounds but also the amount of compounds present in a solid or powder system. Diffraction analysis has advantages over ordinary chemical analysis in that the diffraction method will reveal the presence of compounds whereas chemical analysis can only provide elemental information. Quantitative phase analysis can be used for plasma spray

process development and quality control testing of coatings. Quantitative analysis can be used to determine trace silica in ceramics and minerals, and provide quality control of both of austenite content in heat-treated steel components, and martensite content in mechanically-treated as it reported previously [1]. The method is applied to study of a series of cold-rolled 304 stainless steel plates. The fraction of martensite on the surface

shows an increase as addition in percentage reduction of cold rolling.

The Rietveld method is capable of handling powder diffraction data obtained from X-ray or Neutron diffractometer [2]. In the Rietveld method the least square refinements are carried out until the best fit is obtained between the entire observed (powder) diffraction pattern taken as a whole and the entire calculated pattern based on the simultaneously refined models. Diffraction optic effects [3], instrumental factors, background and other specimen characteristics (e.g. lattice parameters) as may be desired and the peak shape of patterns can be modelled. A key feature is the feedback, during refinement, between improving knowledge of structure and improving allocation of observed intensity to partially overlapping individual Bragg reflections.

The aim of this study is to calculate the quantity of each phase containing in ZrNbMoGe alloys that had been synthesized with various Ge contents by using Rietveld refinement method.

EXPERIMENTAL METHODS

Synthesis of zirconium alloy was carried out by melting the elements of zirconium (Zr sponge), niobium (Nb wire), molybdenum (Mo flake) and germanium (Ge flake), using single arc melting furnace under the argon atmosphere with the temperature more than the melting point of zirconium (1850 °C) [4]. The weight percentage of the elements of the ingot being made was listed in Table 1. All of these elements were melted into the copper crucible which equipped with 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 the 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.

Table 1 shows the compositions of the samples, which have been synthesized in the experiment. Three samples were characterized by high resolution powder diffractometer (HRPD) in neutron scattering laboratory (BSN) PTBIN BATAN to obtain the profiles. The instrument has a wave length of 1.8195 Angstrom, which can penetrate deeply into the materials until equal less than 4 cm [5]. 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 with step of 0.05 degree in the range of 2θ from 2.5 to 100 degree. In the previous work the X-ray diffractograms were obtained as initial study to identify the phases in the samples [6].

RESULTS AND DISCUSSION

Figure 2 shows the neutron diffraction pattern of pure zirconium and its alloy (ZrNbMoGe), obtained by using Neutron Diffractometer ($\lambda = 1.8195\text{\AA}$); (a) ZG0; Pure Zirconium, (b) ZG1; Zircalloy (1 % wt Ge) and (c) ZG2; Zircalloy (3 % wt Ge). The scanning was taken from the angle of $2\theta = 35^\circ$ to 75° , step width of 0.05° and scan mode step counting. The pattern shows good enough in peak to background ratio and all peaks are seen clearly. Figure 2(a) shows that the first five peaks of hexagonal closed packed zirconium arise between the angle of $2\theta = 35^\circ$ and $2\theta = 75^\circ$. Firstly, the peak of $(10\bar{1}0)$ plane is on the angle of $2\theta = 37.92^\circ$, then, second peak at the angle of $2\theta = 41.41^\circ$ is (0002) plane and the highest peaks of zirconium appearing at the angle of $2\theta = 43.42^\circ$ is $(10\bar{1}1)$ plane. Two peaks arise behind them are $(10\bar{1}3)$ and $(10\bar{1}2)$ planes at the angle of $2\theta = 57.39^\circ$ and $2\theta = 68.50^\circ$ respectively.

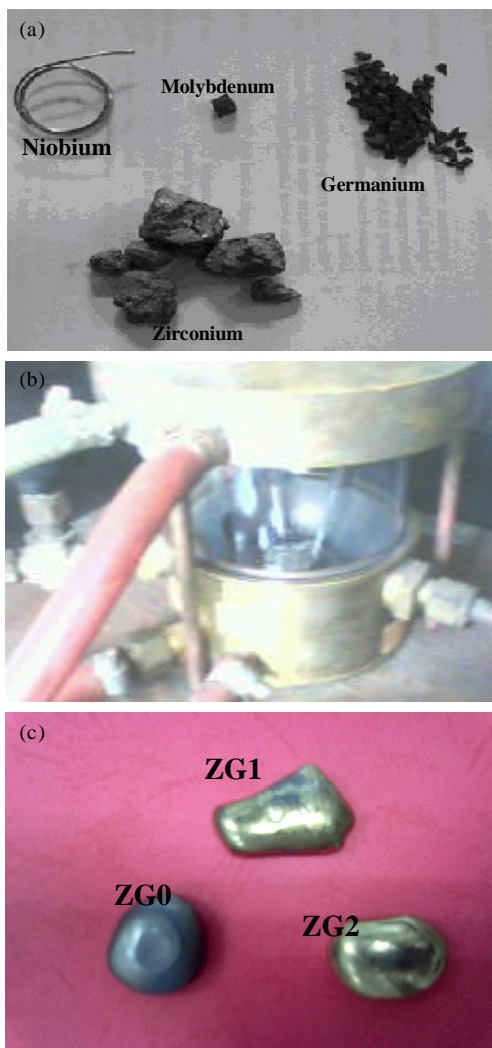


Figure 1. (a). Raw materials, (b). Single Arc Melting Furnace and (c). Pure Zr and ZrNbMoGe ingot.

Table 1. Chemical compositions of the sample.

Sample	Composition of the Elements (%wt)			
	Zr	Nb	Mo	Ge
ZG0	100	-	-	-
ZG1	97,0	1,0	1,0	1,0
ZG2	95,0	1,0	1,0	3,0

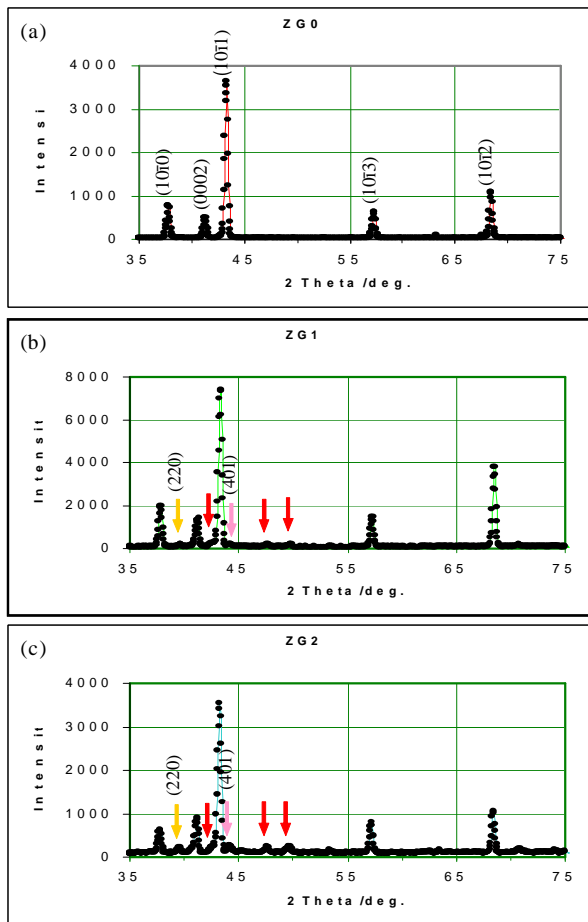


Figure 2. HRPD's profiles of: (a). ZG0; Pure Zirconium, (b). ZG1; Zircalloy (1%wt Ge) and (c). ZG2; Zircalloy (3%wt Ge).

Mean while, there are some peaks grown in between those principal peaks of pure zirconium in Figure 2(b) and 2(c), while the Ge element was added to the intermetallic system of ZrNbMoGe. The red arrows identify the peaks rising in two diffraction profiles bellow.

The peaks belong to $ZrMo_2$, $ZrGe$ and Zr_3Ge phase. Previously we reported that these precipitate arose while the temperature regularly goes down to room temperature [6]. This can also be explained from the phase diagrams in literature [7]. The precipitation formed at 1535 °C to 895 °C is the Zr_3Ge phase and the Zr_2Ge phase (which is not stable) with an orthorhombic structure. So, while the composition of 95 %wt Zr and 2 %wt Ge combined, the precipitation formation was dominated by the Zr_3Ge phase when other precipitates have not been yet formed. Meanwhile, the presence of 2 %wt Mo in the alloy contributes to the formation of the $ZrMo_2$ precipitates with a body centered cubic lattice symmetry.

Table 2 shows the d -spacing calculations resulting from X-ray and neutron diffraction. Both of them are very closed to the reference values of the d -spacing listed in last column. The d -spacing were calculated by utilizing Bragg formula: $\lambda = 2d \sin\theta$. Because of different wavelength of scattered beams, the position of reflection peaks (2θ) in the diffraction pattern will shift neither to higher nor lower of 2θ angle. In this case, the 2θ shifting occurs because of utility of wavelength in X-ray (1.5405Å) and neutron (1.8195 Å) which can move diffraction angle to higher 2θ when wavelength is bigger.

The structure data analysis was performed using the Rietveld Analysis (RIETAN), a Rietveld structure refinement program developed by F. Izumi [8], which is capable of handling powder diffraction data obtained with X-ray or Neutron. In Figure 3, the patterns of the refinement for ZG0, ZG1 and ZG2 specimens are shown. In the profiles, there are several marks of line broadening. The vertical lines below both patterns (raw and model) are indication of zirconium, $ZrGe$, Zr_3Ge phase positions, whereas the line above residual pattern is position of $ZrMo_2$ phase respectively. It can clearly be seen in Figure 2, from (220) and (401) reflections that the minor

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

X-ray ($\lambda = 1.5405\text{\AA}$)				Neutron ($\lambda = 1.8195\text{\AA}$)				Peak of the plane	Ref. $d_{hkl}\text{\AA}$
$2\theta\text{/deg}$	$\sin\theta$	$d_{hkl}\text{\AA}$	Peak of the plane	$2\theta\text{/deg}$	$\sin\theta$	$d_{hkl}\text{\AA}$	Peak of the plane		
32.00	0.2757	2.7933	Zr (10 $\bar{1}$ 0)	37.85	0.3244	2.8039	Zr (10 $\bar{1}$ 0)	2.79	
				39.63	0.3418	2.6834	ZrGe (002)	2.68	
				39.70	0.3397	2.6782	ZrMo ₂ (220)	2.67	
33.60	0.2891	2.6638	Zr ₃ Ge (002)	39.98	0.3418	2.6610	Zr ₃ Ge (002)	2.66	
34.30	0.2979	2.6111	ZrGe (210)	40.65	0.3475	2.6181	ZrGe (210)	2.62	
34.90	0.2999	2.5676	Zr (0002)	41.30	0.3528	2.5787	Zr (0002)	2.57	
35.50	0.3049	2.5255	ZrGe (102)	42.49	0.3625	2.5097	ZrGe (102)	2.52	
36.55	0.3137	2.4554	Zr (10 $\bar{1}$ 1)	43.34	0.3694	2.4628	Zr (10 $\bar{1}$ 1)	2.46	
37.40	0.3207	2.4015	Zr ₃ Ge (202)	44.29	0.3771	2.4125	Zr ₃ Ge (202)	2.40	

Table 3. Initial parameters of the ZrNbMoGe structural refinement.

Crystallographic Data	Zirconium phase			Minor Phases	
	Zr	ZrMo ₂	Zr ₃ Ge	ZrGe	
Formula					
Space Group	P6 ₃ /mmc (I-194)	Im3m (I-229)	P4 ₂ /n (I-86)	Pnma (I-62)	
Lattice Parameter: <i>a</i> (Å)	3.232	7.514	11.299	8.227	
<i>b</i> (Å)	3.232	7.514	11.299	4.189	
<i>c</i> (Å)	5.147	7.514	5.293	5.366	
α, β, γ (deg.)	90,90,120	90,90,90	90,90,90	90,90,90	
Cell Volume (Å ³)	46.690	424.344	675.797	184.928	
Atomic Number in Unit Cell, Z	2	2	2	2	
Atomic Position <i>x, y, z</i>	Zr 1/3 2/3 1/4	Zr 0 0 0	Zr 0 0.106 0.250	Zr 0 0.10 0.25	
		Mo 5/8 5/8 5/8	Ge 0 0.445 0.250	Ge 0 0.75 0.25	

Table 4. Refinement result of ZrNbMoGe structure.

Specimens	Ge Composition (%wt)	R _{wp} (%)	Reliable Factor; S	Lattice Parameters (Å)			
				Zr	ZrMo ₂	ZrGe	Zr ₃ Ge
ZG0	-	12.62	1.24	a= 3.232(0) b= 3.232(0) c= 5.146(0)	-	-	-
ZG1	1.00	15.45	1.53	a= 3.234(0) b= 3.234(0) c= 5.161(0)	a=b=c= 7.512(9)	a= 8.406(1) b= 4.197(3) c= 5.369(0)	a= 11.205(2) b= 11.205(2) c= 5.351(1)
ZG2	3.00	16.39	2.12	a= 3.234(1) b= 3.234(1) c= 5.161(1)	a=b=c= 7.513(1)	a= 8.405(1) b= 4.198(2) c= 5.369(1)	a= 11.205(4) b= 11.205(4) c= 5.351(2)

phase grows as an increase in the percent of Ge element. Since there was no evidence of minor phase in the diffraction patterns, the ZG0 specimen was assumed to be fully hexagonal crystal structure. The refinement was undertaken using a four-phase model consisting of the zirconium phase (hexagonal) with the space group P6₃/mmc (I-194), the ZrGe phase (orthorhombic) with the space group Pnma (I-62), the Zr₃Ge phase (tetragonal) with the space group P4₂/n (I-86) and the ZrMo₂ phase (cubic) using the body centred tetragonal with the space group Im3m (I-229). Initial lattice parameters are predicted in Table 3, which gives the initial refined crystal structure parameters for the specimens.

The peak shape profile of each phase was modelled separately using a pseudo-Voigt function (a linear combination of a Gaussian and a Lorentzian function) [9]. The angular coverage of the experimental data was adequate to allow the structural parameters for each phase to be refined. These include lattice parameters, isotropic thermal parameters, zero point shifts, anisotropic (preferred orientation) parameters and profile parameters. The refinement of this four-phase model was satisfactory enough for each specimen, with the *Rwp* ranging from 12% to 16% (listed in Table 4). The lower *Rwp* cannot be obtained due to the insufficiently statistical data.

Table 5. Fraction of the Phases in ZrNbMoGe.

ZG0 (R _{wp} =12.62%)			ZG1 (R _{wp} =15.45%)			ZG2 (R _{wp} =16.39%)		
Plane	Counts (a.u.)	Fraction of Phase (%)	Plane	Counts (a.u.)	Fraction of Phase (%)	Plane	Counts (a.u.)	Fraction of Phase (%)
Zr (10 $\bar{1}$ 0)	23041		Zr (10 $\bar{1}$ 0)	25346		Zr (10 $\bar{1}$ 0)	16661	
Zr (10 $\bar{1}$ 1)	100000	100	Zr (10 $\bar{1}$ 1)	100000	94.1942	Zr (10 $\bar{1}$ 1)	100000	84.4472
			ZrMo ₂ (220)	828		ZrMo ₂ (220)	1637	
			ZrMo ₂ (311)	2667	2.0548	ZrMo ₂ (311)	5343	4.1656
			ZrGe (002)	1293		ZrGe (002)	2553	
			ZrGe (211)	11	0.5997	ZrGe (211)	17	1.2026
			Zr ₃ Ge (401)	1202		Zr ₃ Ge (401)	4235	
			Zr ₃ Ge (202)	1036	3.1513	Zr ₃ Ge (202)	3613	10.1846

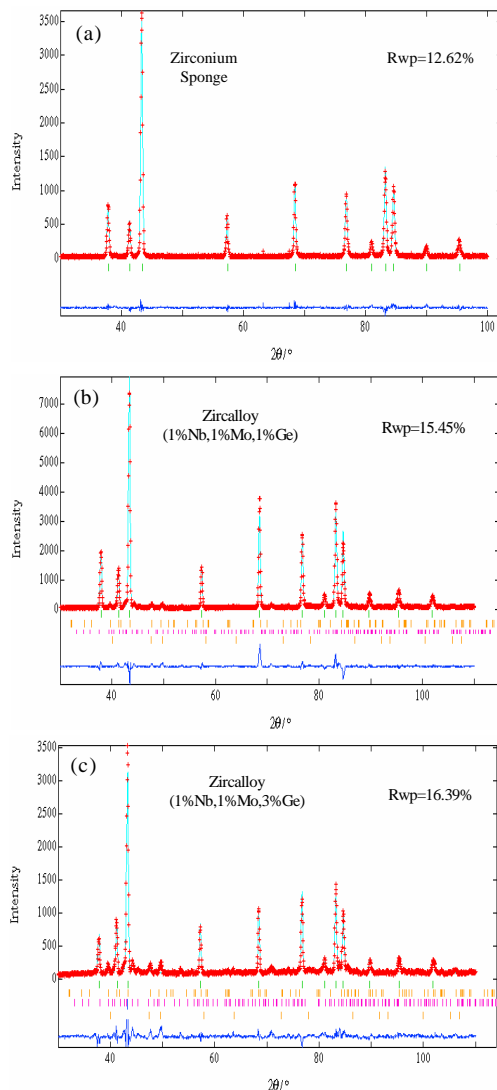


Figure 3. Rietveld refinement profiles of: (a). ZG0; Pure Zirconium, (b). ZG1; Zircalloy (1% wt Ge) and (c). ZG2; Zircalloy (3% wt Ge).

The refined lattice and profile parameters for both the minor phases vary little from specimen to specimen. In addition, reasonable thermal parameters were also obtained from the refinement, which have positive value. A complete set of refined structural parameters was read from data base in the RIETAN software [8]. The data profiles have been calculated by using Rietveld refinements programme successfully and running well. Figure 3 shows the refined structural patterns with the residual appearances that indicate the fitted profiles (model) with the experimental data for three of the specimens; ZG0, ZG1 and ZG2.

A summary of refined lattice parameters, Rwp , and reliable factors is given in Table 4. Meanwhile, Table 5 listed volume fraction of the phases. Figure 4 also illustrated the minor phase growth, predicted by Rietveld refinement analysis. The minor phase fraction can be calculated from scale factor of each phase, using a relation $W_m = (SZV)_m / \sum_i S_i Z_i V_i$, where S, Z, and V are the

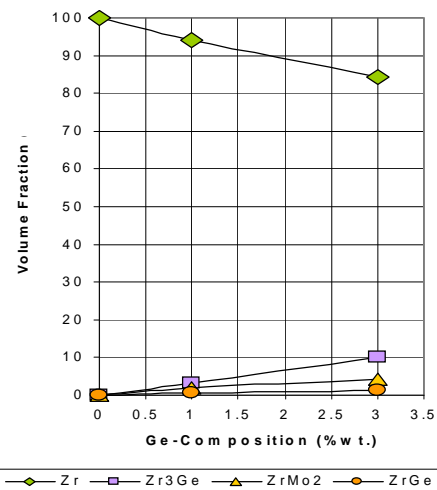


Figure 4. Fraction of the phases in ZG0; Pure Zirconium, ZG1; Zircalloy (1 % wt Ge) and ZG2; Zircalloy (3 % wt Ge).

scale factor, number of formula per unit cell and unit cell volume, respectively. Whereas subscribe m indicate minor phase and i for the phase content in the specimens. The fraction of minor phases on the specimens shows an increase as addition in Ge content. As the phase diagrams predicted above, the proof that Zr_3Ge phase dominated in the precipitation formation is shown in the graph below. The phase rises of about 3% to of about 10% volume fraction while the Ge content increase from 1% wt to 3% wt in the alloys. Otherwise, the zirconium phase regularly decreases from about 94% to of about 84% volume fraction as rising of Ge composition from 1% wt to 3% wt in the alloys.

CONCLUSIONS

It can be concluded that the crystal structure of ZrNbMoGe alloy consists of structure of pure zirconium i.e. hexagonal closed pack (hcp) with lattice parameters of $a = 3.23\text{\AA}$, $b = 3.23\text{\AA}$ and $c = 5.14\text{\AA}$, and the structure of $ZrMo_2$ i.e. body centered cubic (bcc) with lattice parameters of $a = b = c = 7.59\text{\AA}$, and the structure of $ZrGe$ i.e. orthorhombic with lattice parameters of $a = 7.07\text{\AA}$, $b = 3.90\text{\AA}$ and $c = 5.39\text{\AA}$, and the structure of Zr_3Ge i.e. tetragonal (bct) with lattice parameters of $a = b = 11.205\text{\AA}$ and $c = 5.351\text{\AA}$. There is no significantly different information between X-ray and neutron scattering in analyzing the crystal structure of the materials.

The volume fraction of the minor phases on specimens shows an increase as addition in Ge content. The ZG1 specimen contains of: 94.19% wt of Zr phase, 2.05% wt of $ZrMo_2$ phase, 3.15% wt of Zr_3Ge and 0.59% wt of $ZrGe$ phase. Whereas the ZG2 specimen comprises of: 84.45% wt of Zr phase, 4.16% wt of $ZrMo_2$ phase, 10.18% wt of Zr_3Ge and 1.20% wt of $ZrGe$ phase. The data were valid enough due to the obtained Rwp and reliable factors from the refinements of the profiles.

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