Structural refinement of neutron powder diffraction data of *two-stage* martensitic phase transformations in $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ shape memory alloy

Husin Sitepu^{a)}

Crystallography Laboratory, Virginia Tech, Blacksburg, Virginia 24061, USA and Prince Sultan University, P.O. Box 66833, Riyadh 11586, Saudi Arabia

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Transformation behaviors of the technologically important polycrystalline $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ shape memory alloy were investigated using differential scanning calorimeter (DSC) and powder diffraction techniques. DSC revealed that there are *two-stage* (i.e., cubic $\rightarrow$ trigonal $\rightarrow$ monoclinic) martensitic phase transformations on cooling and a one-step transformation (monoclinic $\rightarrow$ cubic) on heating. *In situ* structural refinement of cubic $\rightarrow$ trigonal $\rightarrow$ monoclinic on cooling was carried out using the D1A *high-resolution* neutron powder diffractometer at the Institut Laue-Langevin Neutrons for Science in Grenoble, France. Results showed that the phases involved during the phase transition are consistent with the differential scanning calorimeter cooling curve, and the refined crystal structure parameters obtained from Rietveld refinements with the generalized spherical harmonic description agreed reasonably well with *X-ray single-crystal* data. Subsequently, a combined neutron and synchrotron structural refinement for each phase was conducted because the trial refinements initially using only the synchrotron data of trigonal phase yielded a false minimum with a somewhat high *goodness-of-fit* χ^2 . Results obtained from the combined neutron and synchrotron data of the cubic, trigonal, and monoclinic phases show that the same minimum *goodness-of-fit* indices were always obtained. © 2007 International Centre for Diffraction Data. [DOI: 10.1154/1.2754715]

Key words: neutron powder diffraction, generalized spherical harmonic, shape memory alloy, Ti-Ni, martensitic transformation

I. INTRODUCTION

Shape memory and superelasticity effects in $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ ternary alloy *heat-treated* at 1000 °C for 1 h (Hara *et al.*, 1995, 1997) and Ni-rich $\text{Ti}_{49.3}\text{Ni}_{50.7}$ binary alloy aged at 400 °C for 24 h (Sitepu *et al.*, 2002a) undergo *two-stage* martensitic phase transformations. The phase transformations are from the *high-temperature* cubic structure (or austenite-parent B2 phase) with $Pm\bar{3}m$ space group (No. 221) and $Z=1$ via the trigonal structure (or R-phase) with $P\bar{3}$ space group (No. 147), $Z=9$ at room temperature to a monoclinic structure (or martensitic-B19' phase) with $P112_1/m$ space group (No. 11), and $Z=2$ at low-temperature. Figure 1(a) shows the schematic of the *two-stage* cubic $\rightarrow$ trigonal $\rightarrow$ monoclinic martensitic phase transformations, on cooling, in (1) the *heat-treated* $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ and the aged Ni-rich $\text{Ti}_{49.3}\text{Ni}_{50.7}$ shape memory alloys (left), and (2) $\text{Ti}_{50}\text{Ni}_{30}\text{Fe}_{20}$ (Miyamoto *et al.*, 2005) alloy (right). Also, the figure shows the one-stage phase transformation (middle) in the annealed $\text{Ti}_{49.86}\text{Ni}_{50.14}$ and $\text{Ti}_{49.3}\text{Ni}_{50.7}$ (Sitepu *et al.*, 2002b; Sitepu and Brokmeier, 2004). The martensitic phase transformation is first order, displacive, athermal, and thermoelastic and can be induced by temperature. Therefore, the cubic phase and trigonal and monoclinic phases have the same chemical compositions.

These technologically important polycrystalline $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ and $\text{Ti}_{49.3}\text{Ni}_{50.7}$ alloys are subject to manufacturing processes that impact a crystallographic preferred orientation of the individual crystal grains within the mate-

rial. The orientation of the grains, or polycrystalline texture, can have a profound effect on the physical properties of a manufactured part, affecting both its strength and possible failure modes, and cause serious systematic errors in phase-composition analysis and also in crystal structure refinement (Dollase, 1986; Von Dreele, 1997; Wenk *et al.*, 2001; Sitepu *et al.*, 2004a; Sitepu and Brokmeier, 2005). Therefore, correction of powder diffraction intensities because of the effects of preferred orientation is a vital part to determine the crystal structure of the *two-stage* martensitic phase transformations.

Hara *et al.* (1995, 1997) experimented with electron diffraction and X-ray powder diffraction and showed that (1) addition of the $\text{Fe}_{1.50}$ element yields the trigonal phase, (2) there is no additional peak from the Fe element, and (3) the wire-shaped $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ alloy has a fibered texture with (111) of cubic phase. While the fibered texture information in this alloy proved to be useful information as a qualitative measure of texture [see Figure 1(b)], they did not include the preferred orientation correction in their Rietveld refinements. Therefore, their crystallographic R_p , R_{wp} , and $R(F^2)$ factors and refined crystal structure parameters of trigonal phase in this alloy need further studies because the powder diffraction pattern from a specimen exhibiting the preferred orientation will display intensity values that differ systematically from those of an ideal sample with random orientation (Sitepu *et al.*, 2001; Sitepu, 2002, 2003; Sitepu *et al.*, 2004b). Recently, Sitepu *et al.* (2005a) conducted a comparative evaluation of the March model (Dollase, 1986) and generalized spherical harmonic (GSH) description (Bunge, 1982) for preferred orientation using X-ray diffraction data

^{a)}Electronic mail: sitepu@vt.edu

Figure 1. (a) Three martensitic phase transformation paths in Ni-Ti shape memory alloys. (b) Pole-figures of the first six reflections of the cubic phase in $Ti_{50.75}Ni_{47.75}Fe_{1.50}$ alloy are given in equal area projection and linear scale. The pole-density scale is shown on the right-hand side and given in multiples of a random distribution. The GSH description was used to extract the texture information from a simultaneous refinement with 99 neutron powder diffraction patterns (personal communication with R. B. Von Dreele) held in a variety of orientations in the HIPPO neutron time-of-flight diffractometer at LANSCE.

for molybdate and calcite powders uniaxially pressed at five different pressures with the GSAS (Larson and Von Dreele, 2000) Rietveld program. The Rietveld method is well suited for multiphase diffraction data of *low-crystal-symmetry* materials with many overlapping peaks. The descriptions of the Rietveld refinement programs (i.e., BGMN, DBWS, FullProf, GSAS, LHPM, MAUD, NXD) and links to them can be obtained via the Collaborative Computational Project, Number 14 (CCP14), <http://www.ccp14.ac.uk>. Sitepu *et al.* (2005a) showed that the GSH description, which is generated using selection rules depending on the crystal symmetry of the phase under investigation, generally provided superior *figures-of-merit* [R_p , R_{wp} , and $R(F^2)$] and *goodness-of-fit* (χ^2) compared with the March model results.

In the present study, the author uses a differential scanning calorimeter (DSC) to measure phase transformation temperature of the $Ti_{50.75}Ni_{47.75}Fe_{1.50}$ alloy, showing a *two-*

stage cubic $\rightarrow$ trigonal $\rightarrow$ monoclinic martensitic phase transformation on cooling and *one-step* monoclinic $\rightarrow$ cubic phase transformation on heating [see Figure 2(a)]. In addition, the author uses the high flux neutron source of the Institut Laue-Langevin (ILL) Neutrons for Science in Grenoble, France to measure *in situ* high resolution neutron powder diffraction patterns of the *two-stage* martensitic phase transformations from cubic via trigonal to monoclinic structure in this alloy. The very different neutron scattering properties of Ti (i.e., -3.44×10^{-15} m) and Ni (i.e., 10.30×10^{-15} m) allow site occupancies of these two atoms to be established with far greater reliability than can be achieved with X-ray diffraction. The high resolution neutron powder diffraction data for all data sets of the cubic, trigonal, and monoclinic structures were analyzed independently using the GSAS Rietveld analysis with the GSH description, with reference to its use in correcting intensities for preferred orientation bias. Subse-

quently, combined neutron and synchrotron diffraction data sets for the cubic, trigonal, and monoclinic phases were conducted. This is because the trial refinements initially using only synchrotron diffraction data of the trigonal phase in this alloy [see Figure 2(b)] yielded a false minimum with a somewhat high goodness-of-fit χ^2 (Sitepu, 2003).

II. EXPERIMENTAL

A. Material and differential scanning calorimeter analysis and synchrotron diffraction

The *heat-treated* at 1000 °C for 1 h $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ ternary alloy was produced by the Tonkin Corporation and kindly provided by Professor Takuya Ohba of Shimane University [see Hara *et al.* (1995, 1997), Otsuka and Ren (2005), and references therein]. It should be noted that, on cooling, the composition of this alloy and the heat treatment condition at 1000 °C for 1 h were chosen to obtain the stable trigonal phase at room temperature, and an addition of 1.5 atomic percentage of the Fe element yielded the distinction between the first and second DSC temperature peaks of about 25 °C, which are reasonable for structure refinement of *two-stage* martensitic phase transformations in this alloy. Figure 2(a) depicts the transformation temperatures of this alloy determined by the DSC. DSC results reveal *two-stage* martensitic phase transformations on cooling and *one-stage* phase transformation on heating. The trigonal phase martensitic transformation start temperature and finish temperature are 37 °C and 26 °C, respectively, and the monoclinic phase transformation start and finish temperatures are 11 °C and 25 °C, respectively. There was no change in the appearance of the DSC data when the experiment was repeated. It should be noted that when this alloy is investigated at 23 °C it does really matter if this temperature was reached by cooling from high temperatures (i.e., trigonal) or by heating from low temperatures (i.e., monoclinic)—see Figure 2(a).

The goodness-of-fit χ^2 obtained by Rietveld refinement for all synchrotron diffraction data sets of the single trigonal phase in this alloy from (8±3) °C to (38±3) °C [see Figure 2(b)] were described by Sitepu (2003), which yields a false minimum with a somewhat high value (i.e., 8× exceeding the ideal random powder diffraction value). In the present study, the additional synchrotron diffraction data for the cubic structure at (60±3) °C were measured for 1 h, and data for the monoclinic structure at (−5±3) °C were collected for 6 h [see Figure 2(b)]. Like the trigonal synchrotron diffraction data at (22±3) °C (Sitepu, 2003), the additional cubic and monoclinic data measured in this study were then processed and, combined for each scan to yield a single diffraction data set. Note that the synchrotron diffraction data are (1) pure cubic phase at (60±3) °C, (2) pure trigonal phase at (22±3) °C, (3) a mixture of monoclinic and trigonal phases at (−5±3) °C, and (4) not measured below (−5±3) °C because of a limitation of synchrotron beam time.

B. High resolution neutron powder diffraction measurements

Neutron diffraction data of cubic, trigonal, and monoclinic phases in the $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ shape memory alloy

were measured at the ILL high flux neutron source in Grenoble, France, using the D1A (the D1A instrument is described in the ILL Neutron for Science website, http://www.ill.fr/YellowBookCDrom/data/4_1_1.pdf) *high-resolution fixed-wavelength* neutron powder diffractometer. It should be noted that the cylindrical shape of this alloy, 3 mm in diameter and 9 mm in height, corresponds to the dimensions of the primary beam, which was chosen using an appropriate collimation. During neutron diffraction data collection, the D1A instrument was equipped with a cryofurnace to heat and cool the alloy (with a temperature constant zone exceeding the length of the rod alloy). The angular 2θ working range was from 3 deg to 159 deg (25 detectors of type ^3He with 6 deg angular range each). Experiments were performed using a neutron wavelength of 1.9114(1) Å and an angular step size of 0.05 deg. After mounting the alloy in the ILL cryofurnace, the alloy was carefully heated to the cubic structure at a temperature of (113±3) °C. Prior to the neutron diffraction experiments, the alloy was held at 113 °C for 6 min so that a thermal-equilibrium condition could be reached. The alloy temperature was then slowly cooled down to (60±3) °C (i.e., the pure cubic structure), and the neutron diffraction data were measured for 2 h. The sample was not spun during the data collection because it was fixed at the cryofurnace. After that, the sample temperature was slowly cooled down to (22±3) °C, which is the pure trigonal structure, and the neutron diffraction data were measured for 7 h. Finally, the alloy temperature was slowly cooled down to (−253±3) °C, which is the pure monoclinic phase, and the neutron diffraction data were measured for 11 h. The data from the 25 detectors were then processed and combined to yield a single diffraction pattern using interpolations between adjacent observations to correct for *zero-point* offsets and detector sensitivities. Figure 2(c) shows neutron powder diffraction data are consistent with the DSC results on cooling.

C. Structural refinement using Rietveld method

The structural refinements of neutron diffraction data for cubic, trigonal, and monoclinic were conducted using the GSAS Rietveld analysis with the GSH description (Bunge, 1982; Popa, 1992; Von Dreele, 1997). The cubic, trigonal, and monoclinic structural models were described by Wang *et al.* (1965), Schryvers and Potapov (2002), and Kudoh *et al.* (1985), respectively. The refinement strategy was first to refine the phase scale factor and the background component of the patterns with a six parameter Chebychev polynomial, followed by adding lattice parameters and zero-point $2\theta_0$ to the refinement, then the Lorentzian and Gaussian terms of the pseudo-Voigt profile function, and the anisotropic strain (Popa, 1998; Stephens, 1999) parameters together with the structural parameters including atomic parameters, isotropic temperature factors, and site occupancies. After the refinement converged, the GSH coefficients were finally added to the refinement. The sample texture symmetry was chosen to be cylindrical, and a maximum six harmonic orders were selected (preliminary calculations with eight orders gave the same results). Subsequently, the combined neutron and synchrotron structural refinement was conducted for each phase.

Figure 2. (a) DSC curves for the *two-stage* martensitic phase transformations on cooling and *one-stage* transformation on heating in $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ alloy. (b) *In situ* synchrotron structure of cubic ($60 \pm 7^\circ\text{C}$), trigonal (from 38.5 to $8 \pm 7^\circ\text{C}$), and the mix of monoclinic and trigonal ($-5 \pm 7^\circ\text{C}$), on cooling. (c) *In situ* neutron diffraction structure of cubic ($60 \pm 3^\circ\text{C}$), trigonal ($22 \pm 3^\circ\text{C}$), and monoclinic ($-253 \pm 3^\circ\text{C}$) during cooling from high temperature.

III. RESULTS AND DISCUSSION

Figure 2(a) shows that there are two distinct DSC peaks in the $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ shape memory alloy (i.e., *two-stage* cubic $\rightarrow$ trigonal $\rightarrow$ monoclinic martensitic phase transformations) on cooling, and a *one-step* monoclinic $\rightarrow$ cubic phase transformation on heating. In addition, when this alloy is investigated at room temperature, it consists of the trigonal

structure if this temperature was reached by cooling from high temperatures or the monoclinic structure by heating from low temperatures [see Figure 2(a)]. The pole-figure results obtained from Rietveld refinement with GSH description for all 99 neutron diffraction (personal communication with R. B. Von Dreele) data sets of the cubic structure at various orientations are given in Figure 1(b). The figure

TABLE I. Refined crystal structure parameters for cubic phase in the $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ alloy at a temperature of $(60 \pm 3)^\circ\text{C}$. The space group used was $Pm\bar{3}m$ (No. 221). GOFI=goodness-of-fit index, f =site occupancy, SRD=synchrotron diffraction, ND=neutron diffraction, and N/A=not available.

Refined parameters ^a		Atomic parameters			
		Wang <i>et al.</i> (1962)	This study		
			Synchrotron ^b	Neutron	Combined
a (Å)		3.01	3.0297(18)	3.02(5)	3.0191(12)
$\text{Ti}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	f	N/A	0.9206(23)	1.023(7)	0.9419(18)
	Uiso (Å) ²	N/A	0.01115(20)	0.0461(9)	0.01174(14)
$\text{Ni}(0,0,0)$	f	N/A	1.0233(23)	0.977(7)	1.0581(18)
	Uiso (Å) ²	N/A	0.01115(20)	0.0461(9)	0.01174(14)
Figures-of-merit and GOFI index					
	R_p	N/A	6.43	6.76	8.27 [SRD] 14.57 [ND]
	R_{WP}	N/A	8.84	8.70	11.93 [SRD] 20.11 [ND]
	$R(F^2)$	N/A	5.47	2.03	7.54 [SRD] 1.92 [ND]
	χ^2	N/A	15.01	1.12	1.03

^aWyckoff coordinates, $1(a)=0,0,0$; $1(b)=\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

^bSynchrotron diffraction data described by Sitepu (2003)—see Figure 2(b).

shows that this alloy has textured with maximum pole figures of two times a random distribution (note that the pole-figure value is unity for ideal random powder diffraction data). Therefore, crystallographic preferred orientation needed to be included in the refinement of all neutron powder diffraction data sets of this alloy because preferred orientation can cause serious systematic errors not only in crystal structure refinement but also in phase composition analysis (see below).

The refined crystal structure parameters derived from Rietveld refinement with the GSH description for cubic, trigonal, and monoclinic structures are given in Tables I, II, and IV, respectively. Table III shows the deviation of the atomic coordinates for the trigonal phase from the positions in the parent cubic structure. Comparison of the Rietveld fits in Figure 3, where neutron and synchrotron data are both plotted with the same d -spacing, shows that the peak intensities are quite different in the neutron and synchrotron diffraction data sets, because the neutron has a negative scattering length for Ti. Therefore, when combined neutron and synchrotron refinements were used, there is excellent discrepancy between the two atomic sites.

A. Cubic crystal structure

A high-temperature single-crystal X-ray diffraction study reported by Wang *et al.* (1965) reveals a cubic austenite structure (the parent B2 phase) at above the martensitic transformation starting temperature for the Ti-Ni binary alloy with $a=3.01$ Å, space group $Pm\bar{3}m$ (No. 221), Ni atoms occupying the $1a$ (0, 0, 0) Wyckoff positions, and Ti atoms occupying the $1b$ (0.5, 0.5, 0.5) positions (see Table I). However, no isotropic temperature factors are reported.

In this study, the results obtained from Rietveld refinement with the GSH description for neutron and synchrotron

powder diffraction data of the cubic phase in $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ alloy at $(60 \pm 3)^\circ\text{C}$ agree reasonably well with single-crystal X-ray diffraction data reported by Wang *et al.* (1965). The Ni and Ti isotropic temperature factors (Uiso) for neutron diffraction data are approximately four times higher than those of the corresponding synchrotron values. The neutron site occupancy value for Ti is higher than that of the synchrotron, whereas the corresponding site occupancy value for Ni is vice versa. While the neutron crystallographic R_{WP} and R_p factors are almost the same as those of the synchrotron, both the crystallographic $R(F^2)$ and goodness-of-fit χ^2 values for the neutron are far superior to that of the synchrotron. This indicates that the refinement using only the single synchrotron data found a false minimum with somewhat worse χ^2 than those of neutron diffraction data. When combined neutron and synchrotron powder diffraction data sets were used in Rietveld refinements, practically the same minimum χ^2 was always obtained. It should be noted that, while the combined refinement provides the neutron $R(F^2)$ value superior to that of the synchrotron data, the R_{WP} and R_p values for the neutron are vice versa. Figure 3 shows the results of the Rietveld fits for the cubic phase at $(60 \pm 3)^\circ\text{C}$. Because the scattering factor for Ti is -3.44×10^{-15} m, the peak intensities are quite different in both the synchrotron and neutron diffraction data sets. Therefore, a combined structural refinement of both synchrotron and neutron diffraction data sets is an excellent way to determine the crystal structures of the $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ alloy.

B. Trigonal crystal structure

Schryver and Patapov (2002), Sitepu (2003), and Sitepu *et al.* (2005b) reported that no significant improvement in Rietveld fit was found when the inversion center was re-

TABLE II. Refined crystal structure parameters for the trigonal phase in the $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ alloy at a temperature of $(22 \pm 3)^\circ\text{C}$. The space group used was $P\bar{3}$ (No. 147). GOFI=goodness-of-fit index, f =site occupancy, SRD=synchrotron diffraction, ND=neutron diffraction, and N/A=not available.

Refined parameters ^a		Atomic parameters			
		Schryvers and Potapov (2002)	This study		
			Synchrotron ^b	Neutron	Combined
a (Å)		7.3472(2)	7.37607(5)	7.34(19)	7.3715(32)
c (Å)		5.2837(3)	5.30520(5)	5.28(14)	5.3020(23)
Ti(0,0,0)	f	N/A	0.866(4)	1.144(34)	0.885(4)
	Uiso (Å) ²	N/A	0.009 06(35)	0.0503(31)	0.00915(28)
Ni(0,0, $\frac{1}{2}$)	f	N/A	1.000	1.000	1.000
	Uiso (Å) ²	N/A	0.008 53(32)	0.0378(9)	0.00641(26)
Ti(x,y,z)	x	−0.013	−0.010 68(28)	−0.0068(14)	−0.00864(24)
	y	0.331	0.3328(4)	0.3174(30)	0.3242(4)
	z	0.679	0.656 23(32)	0.6605(16)	0.65670(26)
	f	N/A	0.866(4)	1.144(34)	0.885(4)
	Uiso (Å) ²	N/A	0.009 06(35)	0.0503(31)	0.00915(28)
Ni(x,y,z)	x	−0.001	−0.017 64(21)	−0.0185(5)	−0.01872(19)
	y	0.325	0.319 52(29)	0.3190(11)	0.32588(31)
	z	0.148	0.146 97(27)	0.1444(7)	0.14702(23)
	f	N/A	1.000	1.000	1.000
	Uiso (Å) ²	N/A	0.008 53(32)	0.0378(9)	0.00641(26)
Ti($\frac{1}{3}, \frac{2}{3}, z$)	z	0.045	0.0289(4)	0.0332(22)	0.0299(4)
	f	N/A	0.866(4)	1.144(34)	0.885(4)
	Uiso (Å) ²	N/A	0.009 06(35)	0.0503(31)	0.00915(28)
Ni($\frac{1}{3}, \frac{2}{3}, z$)	z	0.547	0.5647(4)	0.5632(9)	0.5656(4)
	f	N/A	1.000	1.000	1.000
	Uiso (Å) ²	N/A	0.008 53(32)	0.0378(9)	0.00641(26)
Figures-of-merit and GOFI index					
	R_p	N/A	5.04	4.85	5.15 [SRD] 7.44 [ND]
	R_{WP}	N/A	7.39	5.95	7.14 [SRD] 9.75 [ND]
	$R(F^2)$	N/A	8.08	3.56	7.83 [SRD] 5.85 [ND]
	χ^2	N/A	6.78	1.91	4.88

^aWyckoff coordinates, 1(a)=0,0,0; 1(b)=0,0, $\frac{1}{2}$; 2(d)= $\frac{1}{3}, \frac{2}{3}, z$; 6(g)= x,y,z .

^bSynchrotron diffraction data described by Sitepu (2003)—see Figure 2(b).

moved from the $P\bar{3}$ model. This suggests that the space group for the trigonal structure in the $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ alloy after cooling to room temperature was indeed $P\bar{3}$, not lower symmetry $P3$ or $P31m$. In addition, the refined atomic parameters for all synchrotron diffraction data sets of the trigonal phase were converging only when the $P\bar{3}$ space group was used in the Rietveld refinement (Sitepu, 2003; Sitepu *et al.*, 2005b).

In the present study, the results obtained from Rietveld refinement with GSH description for (1) single neutron, (2) single synchrotron, and (3) combined neutron and synchrotron diffraction data of trigonal structure at $(22 \pm 3)^\circ\text{C}$, on cooling, are given in Table II. The values in parentheses are estimated standard deviations. The refined atomic parameters for synchrotron data agree reasonably well with the transmission electron microscope results reported by Schryver and Patapov (2002). The neutron Ti atomic site occupancy (f)

TABLE III. Deviations of the atomic co-ordinates for the combined neutron and synchrotron diffraction data sets of trigonal (or R -phase) at a temperature of $(22 \pm 3)^\circ\text{C}$ from the positions in the parent cubic (or B2) structure. The space group used was $P\bar{3}$ (No. 147).

Deviation from the positions of the parent cubic structure			
Parameters ^a	Δx	Δy	Δz
Ti(0,0,0)	—	—	—
Ni(0,0, $\frac{1}{2}$)	—	—	—
Ti(x,y,z)	−0.008 64	−0.0091	−0.009 66
Ni(x,y,z)	−0.018 72	−0.009 66	0.022 02
Ti($\frac{1}{3}, \frac{2}{3}, z$)	—	—	0.0299
Ni($\frac{1}{3}, \frac{2}{3}, z$)	—	—	0.063 83

^aWyckoff coordinates, 1(a)=0,0,0; 1(b)=0,0, $\frac{1}{2}$; 2(d)= $\frac{1}{3}, \frac{2}{3}, z$; 6(g)= x,y,z .

TABLE IV. Refined crystal structure parameters for mix of monoclinic and trigonal phases at $(-5 \pm 7)^\circ\text{C}$ for synchrotron and at $(-253 \pm 3)^\circ\text{C}$ for neutron. The space groups used were $P112_1/m$ (No. 11) for monoclinic and $P\bar{3}$ (No. 147) for trigonal. GOFI=goodness-of-fit index, f =site occupancy, SRD=synchrotron diffraction, ND=neutron diffraction, and Wt(%)=weight percentage of monoclinic and trigonal phase for synchrotron data only.

Refined parameters ^{a,b}		Atomic parameters			
		Kudoh <i>et al.</i> (1985)	This study		
			Synchrotron ^c	Neutron	Combined
Monoclinic phase					
a (Å)		2.898(1)	2.8886(1)	2.8731(7)	2.92617(14)
b (Å)		4.108(2)	4.1224(3)	4.0905(7)	4.17272(10)
c (Å)		4.646(3)	4.6453(4)	4.6465(10)	4.69631(25)
β (°)		97.78(4)	97.505(4)	98.165(20)	97.4036(35)
$\text{Ti}(x, y, \frac{1}{4})$	x	0.5824(5)	0.5995(2)	0.582(6)	0.5822(9)
	y	0.2836(3)	0.309(1)	0.2891(35)	0.2884(8)
	f	N/A	0.984(4)	0.920(18)	0.921(4)
	Uiso (Å) ²	0.0107	0.0186(5)	0.0019(21)	0.0100(4)
$\text{Ni}(\bar{x}, \bar{y}, \frac{3}{4})$	x	0.0372(4)	0.0139(10)	0.0354(20)	0.0260(8)
	y	0.1752(2)	0.1504(9)	0.1739(11)	0.1757(6)
	f	N/A	1.078(10)	1.080(18)	1.079(4)
	Uiso (Å) ²	0.0126	0.0127(4)	0.0019(21)	0.0100(4)
Trigonal phase		Schryvers and Potapov (2002)			
a (Å)		7.3472(2)	7.3681(8)		7.378 34(2)
c (Å)		5.2837(3)	5.3135(6)		5.320 89(4)
$\text{Ti}(0,0,0)$	f	N/A	0.871(4)		0.885(4)
	Uiso (Å) ²	N/A	0.0115(5)		0.009 15(28)
$\text{Ni}(0,0,\frac{1}{2})$	f	N/A	1.000		1.000
	Uiso (Å) ²	N/A	0.0068(4)		0.006 41(26)
$\text{Ti}(x, y, z)$	x	-0.013	-0.0125(5)		-0.0086 64(24)
	y	0.331	0.3247(7)		0.3242(4)
	z	0.679	0.6533(6)		0.656 70(26)
	f	N/A	0.871(4)		0.885(4)
$\text{Ni}(x, y, z)$	Uiso (Å) ²	N/A	0.0115(5)		0.009 15(28)
	x	-0.001	-0.017 12(35)		-0.018 72(19)
	y	0.325	0.3283(5)		0.325 88(31)
	z	0.148	0.1497(5)		0.147 02(23)
$\text{Ti}(\frac{1}{3}, \frac{2}{3}, z)$	f	N/A	1.000		1.000
	Uiso (Å) ²	N/A	0.0068(4)		0.006 41(26)
	z	0.045	0.0318(7)		0.0299(4)
	f	N/A	0.871(4)		0.885(4)
$\text{Ni}(\frac{1}{3}, \frac{2}{3}, z)$	Uiso (Å) ²	N/A	0.0115(5)		0.009 15(28)
	z	0.547	0.5703(7)		0.5656(4)
	f	N/A	1.000		1.000
	Uiso (Å) ²	N/A	0.0068(4)		0.006 41(26)
Figures-of-merit and GOFI index					
	R_p	N/A	5.58	9.46	4.73 [SRD] 15.98 [ND]
	R_{wp}	N/A	7.87	11.70	6.58 [SRD] 20.70 [ND]
	$R(F^2)$	N/A	8.86	4.20	5.80 [SRD] 12.80 [ND]
	χ^2	N/A	7.14	1.19	4.38
Wt(%) for					
• monoclinic			38.55 [SRD]	100.00 [ND]	37.47 [SRD] 100.00 [ND]
• trigonal			61.45 [SRD]	0.00 [ND]	62.52 [SRD] 0.00 [ND]

^aWyckoff coordinates, $2(e)=x, y, \frac{1}{4}$; $2(e)=\bar{x}, \bar{y}, \frac{3}{4}$ for monoclinic.

^bWyckoff coordinates, $1(a)=0, 0, 0$; $1(b)=0, 0, \frac{1}{2}$; $2(d)=\frac{1}{3}, \frac{2}{3}, z$; $6(g)=x, y, z$ for trigonal.

^cSynchrotron diffraction data described by Sitepu (2003)—see Figure 2(b).

value is higher than that of the synchrotron, while the Ti and Ni isotropic temperatures (U_{iso}) for the neutron are less than those for the synchrotron. Results obtained from the combined refinement show (1) the Ti site occupancy value and the Ni isotropic temperature factor are between the synchrotron and neutron values and (2) the isotropic temperature factor for Ti has a discernible decimal change from synchrotron refinement only. In addition, the results show that the neutron diffraction data provide superior the crystallographic R_{WP} and R_p factors compared to that of the synchrotron data for the trigonal phase. However, when the combined neutron and synchrotron refinement was conducted, it provided a goodness-of-fit χ^2 lower than that of the synchrotron data refinement only. This result confirms the conclusions for the cubic phase indicating that the same minimum goodness-of-fit was always recovered when combined neutron and synchrotron data sets was used whereas the refinement using only the synchrotron data originally conducted by Sitepu (2003) sometimes found a false minimum with somewhat high goodness-of-fit value.

The results obtained from combined neutron and synchrotron diffraction data of the trigonal phase at $(22 \pm 3)^\circ\text{C}$ confirm the previous study conducted by Sitepu (2003) that $P\bar{3}$ is the right space group. All eight atomic parameters converged and the R_{WP} and $R(F^2)$ values are 7.14 and 7.83 for the synchrotron and 9.75 and 5.85 for the neutron, respectively. In comparison, the crystallographic R_{WP} and $R(F^2)$ factors reported by Hara *et al.* (1995, 1997) with 17 positional parameters for the trigonal phase of $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ were 8.47 and 23.83, respectively. Their $R(F^2)$ value of 23.83 obtained from X-ray powder diffraction data is twice higher than that obtained from the combined synchrotron and neutron fits. This shows that preferred crystallographic orientation should be taken with great care in order to obtain accurate structure refinement results. Therefore, it can be concluded that the combined synchrotron and neutron structural study for the trigonal phase in the $P\bar{3}$ model provides accurate crystal structure parameters when applying corrections to the experimental intensities using the GSH description.

Table III shows the deviation of the trigonal atomic coordinates from the position in the parent cubic phase (or B2) structure. While the deviations of the z coordinate from the $\text{Ti}(x, y, z)$ and $\text{Ti}(\frac{1}{3}, \frac{2}{3}, z)$ atoms in the parent cubic structure are $-0.00966c$ and $0.0299c$, respectively, the $\text{Ti}(x, y, z)$ shift value is very small. The corresponding deviation of z coordinates for the $\text{Ni}(x, y, z)$ and $\text{Ni}(\frac{1}{3}, \frac{2}{3}, z)$ are $0.02202c$ and $0.06383c$, respectively, which are twice higher than that of the $\text{Ti}(x, y, z)$ and $\text{Ti}(\frac{1}{3}, \frac{2}{3}, z)$ atoms. These z -coordinate deviations for $\text{Ti}(x, y, z)$, $\text{Ti}(\frac{1}{3}, \frac{2}{3}, z)$, $\text{Ni}(x, y, z)$, and $\text{Ni}(\frac{1}{3}, \frac{2}{3}, z)$ are smaller than those reported by Hara *et al.* (1995) and Schryvers and Potapov (2002).

C. Monoclinic crystal structure

Kudoh *et al.* (1985) reported that single-crystal X-ray crystal-structure analysis of the monoclinic (or martensitic-B19' phase) in $\text{Ni}_{49.2}\text{Ti}_{50.8}$ alloy with unit-cell parameters of $a=2.898(1)\text{ \AA}$, $b=4.108(2)\text{ \AA}$, $c=4.646(3)\text{ \AA}$, and $\gamma=97.78(1)^\circ$. The space group was $P112_1/m$ (No. 11), which

agreed well with the result published by Michal and Sinclair (1981). Ti atoms occupied $2e$ (0.5824, 0.2836, 0.25) Wyck-off positions and Ni atom were at $2e$ (0.0372, 0.1752, 0.75).

Table IV shows the monoclinic crystal-structure parameters determined from Rietveld refinement with GSH description for neutron diffraction data at $(-253 \pm 3)^\circ\text{C}$ and synchrotron diffraction data at $(-5 \pm 3)^\circ\text{C}$. The values in parentheses are estimated standard deviations. The neutron diffraction data reveal a pure monoclinic phase, whereas synchrotron data show a mixture of monoclinic and trigonal phases. This indicated that the parent structure has not fully transformed to monoclinic at $(-5 \pm 3)^\circ\text{C}$ [see Figures 2(a) and 2(b)]. The cell parameters agree reasonably well with X-ray single-crystal results reported by Kudoh *et al.* (1985). The refined monoclinic atomic parameters for single neutron, single synchrotron, and combined refinement agree reasonably well with the X-ray single-crystal results reported by Kudoh *et al.* (1985). The neutron $\text{Ti}(x, y, \frac{1}{4})$ and $\text{Ni}(\bar{x}, \bar{y}, \frac{3}{4})$ atoms have values for both site occupancies and isotropic temperature factors lower than the synchrotron data. In addition, when the combined refinement was conducted, the $\text{Ti}(x, y, \frac{1}{4})$ and $\text{Ni}(\bar{x}, \bar{y}, \frac{3}{4})$ site occupancies and isotropic temperature factors are between the single synchrotron refinement results and neutron values. Moreover, the refined trigonal atomic parameters for single synchrotron diffraction data and also for the combined refinement neutron and synchrotron data sets agree reasonably well with the results published by Schryver and Popatov (2002).

While the neutron crystallographic $R(F^2)$ and goodness-of-fit χ^2 values for the monoclinic provide superior results compared to those of the single synchrotron data, the crystallographic R_p and R_{WP} factors for the neutron are worse than the synchrotron data. When the combined refinement was conducted, it provided a χ^2 value lower than that of the single synchrotron data. This result confirms the conclusions for the cubic and trigonal phases in which practically the same χ^2 minimum was always obtained when a combined refinement was conducted. On the other hand, the refinement using only the synchrotron data sometimes found a false minimum with somewhat high χ^2 . Since the neutron diffraction data at $(-273 \pm 3)^\circ\text{C}$ consists of a single monoclinic phase [see Figures 2(c) and 3(b)], the neutron crystallographic R_p , R_{WP} , and $R(F^2)$ figures-of-merit are higher than those of the synchrotron because the synchrotron diffraction data consist of a mixture of monoclinic and trigonal phases [see Figures 2(b) and 3(a)].

The weight percentages of monoclinic and trigonal phases are 38.55 and 61.45 for the synchrotron and 100.00 and 0.00 for the neutron, respectively. The corresponding monoclinic and trigonal weight percentages obtained from the combined refinement are 37.47 and 62.52 for the synchrotron and 100.00 and 0.00 for the neutron, respectively. Therefore, it can be concluded that the GSH description can be used successfully to correct the neutron diffraction intensities attributable to the effects of preferred orientation for the purposes of determining crystal-structure information and phase-composition analysis of the *two-stage* martensitic phase transformations.

Figure 3. Comparison of Rietveld fits of (a) synchrotron and (b) neutron diffraction patterns for cubic, trigonal, and monoclinic phases in $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ alloy are plotted at the same d -spacing. The observed data are indicated by plus signs, and the calculated profile is the continuous line in the same field. The lower plot is the difference between the measured and calculated patterns on the same scale as the measured and calculated patterns.

IV. CONCLUSIONS

The present study investigates the phase transition behaviour of technologically important polycrystalline $\text{Ti}_{50.75}\text{Ni}_{47.75}\text{Fe}_{1.50}$ shape memory alloy using DSC, and *in situ* crystal structure determination of phases involved on cooling using Rietveld refinement with GSH description for preferred orientation in neutron and combined neutron and synchrotron data. The following conclusions can be drawn:

The DSC results showed that this alloy has two-stage cubic $\rightarrow$ trigonal $\rightarrow$ monoclinic martensitic phase transformations on cooling and a one-stage monoclinic $\rightarrow$ cubic phase transformation on heating.

The preliminary texture results obtained in this study [see Figure 1(b)] show that this alloy has a texture where the maximum pole-figures are two times *multiple-of-random* distribution. Thus, the preferred orientation correction must be

taken with great care in determining the crystal structure of neutron powder diffraction data of two-stage martensitic phase transformations on cooling.

In situ neutron diffraction data sets of cubic, trigonal, and monoclinic structures are consistent with the DSC cooling curve [see Table IV and Figures 2(a)–2(c)].

The refined crystal structure parameters for neutron diffraction data of cubic, trigonal, and monoclinic agreed quite satisfactorily with X-ray single-crystal data (see Tables I, II, and IV). Therefore, the GSH description can be used for correction of preferred orientation in neutron diffraction data analysis for both *crystal-structure* refinement and *phase-composition* analysis.

When combined neutron and synchrotron structural refinements of cubic, trigonal, and monoclinic were conducted (see Tables I, II, and IV), the same minimum goodness-of-fit χ^2 was always recovered, whereas trial refinements initially

conducted by Sitepu (2003) using the single synchrotron data sometimes found a false minimum with a somewhat worse goodness-of-fit.

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