



Experiment title:

R-phase structure refinement using synchrotron diffraction data

Experiment number:

ME369

Beamline:

ID11 & ID31

Date of experiment:

from: 26 June 2002 to: 27 June 2002

Date of report:

23 December 2004

Shifts:

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Report:

The R-phase in $Ti_{50.75}Ni_{47.75}Fe_{1.50}$ shape memory alloy has been widely used in both industrial and fundamental research because this alloy has shape memory effect or superelasticity and also small thermal hysteresis which are very useful for actuators applications. It occurs in simple system from *high-temperature* cubic (B2) structure to a monoclinic (B19') *low-temperature*, with the trigonal R-phase occurring in an intermediate temperature range, depending on the thermomechanical history of the alloy [1 and references therein], see Fig. 1.

In order to understand the mechanism of the transformation, it is necessary to know the crystal structures of the R-phase. Originally, crystal structure determinations relied mainly on single crystal diffraction data. However, sufficiently large R-phase single crystal is not available and powders have to be used. It is possible to extract preferred crystallographic orientation (PO) information from such powder diffraction data if the pattern for a randomly oriented specimen can be modelled, or simulated, from knowledge of the crystal structure parameters and various other factors (e.g. line broadening due to size and strain parameters) which influence the pattern. The Rietveld refinement with the generalized spherical harmonic (GSH) description generally provided superior figures-of-merit compared with the March model results [2,3]. Therefore, it was concluded that the GSH approach should be used for PO correction in powder diffraction data analysis, for both crystal structure refinement and phase composition analysis. In the present study, (i) the third generation synchrotron X-ray sources, which make available X-ray beams of higher energy and much higher intensity than laboratory X-ray sources, has been used for measuring the synchrotron powder diffraction (SRD) data of $Ti_{50.75}Ni_{47.75}Fe_{1.50}$ alloy and (ii) the GSH description was used to analyze the data. To the best of our knowledge there has been no detailed analysis published in the literature providing information on the R-phase structure refinement using SRD data.

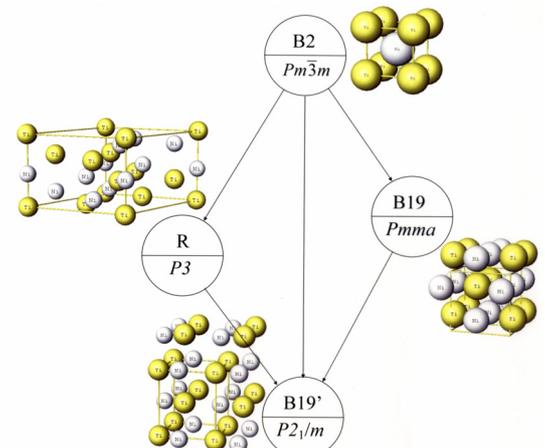


Fig. 1. The martensitic transformations

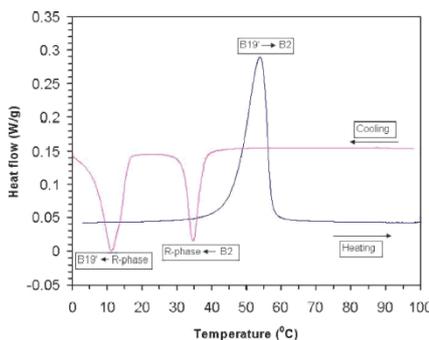


Fig. 2. DSC curve of R-phase in $Ti_{50.75}Ni_{47.75}Fe_{1.50}$ alloy

The rod shaped $Ti_{50.75}Ni_{47.75}Fe_{1.50}$ ternary alloy used in the present study has a diameter of 10 mm and 30 mm height. The alloy was heat-treated at 1273 K. During thermal cycling, the differential scanning calorimeter (DSC) results provided the Martensite starting (M_s) and finishing (M_f) transformation temperatures at (i) $M_s = 310$ K and $M_f = 299$ K for the trigonal R-phase and (ii) $M_s = 284$ K and $M_f = 248$ K for the monoclinic (B19'), see Fig. 2.

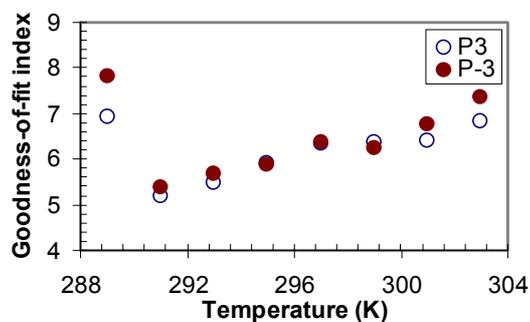


Fig. 3. Variation in goodness-of-fit index with temperature.

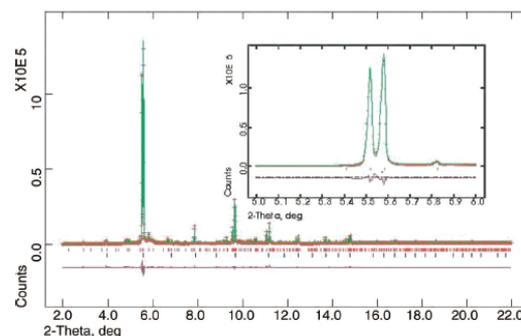


Fig. 4. The agreement between measured and calculated patterns at 297K, on cooling.

Step-scanned patterns were measured using the ESRF ID11 and ID31 high resolution powder diffractometer with the energy of 60 keV ($\lambda = 0.2069 \text{ \AA}$). After mounting the alloy in the diffractometer it was heated up to $(373 \pm 7) \text{ K}$. Then, the temperature was held for 360 s to reach the thermal equilibrium and the data were measured for 4 hours. The temperature was then slowly cooled down to $(301 \pm 7) \text{ K}$ and held for 360 s. Then, the first SRD data was collected. Hold periods for 360 s were conducted to each of the subsequent SRD data collection at temperatures indicated in Fig. 3. The 2θ scan range was three scans from 2° to 22° each at a slightly rock in phi with a 2θ step size of 0.008° , and a total counting time of approximately 4 hours for each temperature. The data were then bin for each scan to yield a single histogram.

Table 1. Deviation of the atomic co-ordinate for the R-phase SRD data at $(297 \pm 7) \text{ K}$ from the positions in the parent cubic (B2) structure. Co-ordinates, $1(a) = 0, 0, 0$; $1(b) = 0, 0, 1/2$; $2(d) = 1/3, 2/3, z$; $6(g) = x, y, z$

Parameters	Wyckoff code	x	y	z	Deviation from the positions in the parent B2 structure		
					Δx	Δy	Δz
Ti1	1(a)	0	0	0	-	-	-
Ti2	2(d)	1/3	2/3	0.031(3)	-	-	0.031
Ti3	6(g)	0.332(4)	-0.007(2)	0.342(2)	-0.001	-0.007	0.009
Ni1	1(b)	0	0	1/2	-	-	-
Ni2	2(d)	1/3	2/3	0.565(3)	-	-	0.0065
Ni3	6(g)	0.322(3)	-0.020(2)	0.854(2)	-0.011	-0.020	0.021

The results obtained from Rietveld refinement with the GSH description for PO correction [2,3] of the all R-phase SRD data sets (e.g. from $(303 \pm 7) \text{ K}$ to $(283 \pm 7) \text{ K}$, on cooling) indicated that: (i) for texture in SRD data sets of R-phase the reasonable crystal structure parameters (see Table 1) and good agreement between measured and calculated patterns (see Fig. 4) were obtained when applying correction to intensities using the GSH description, (ii) the weight percentage of the non-transformed austenite was approximately 3%, and (iii) no significant improvement in goodness-of-fit index was found (see Fig. 3) when the inversion center was removed from the $P\bar{3}$ model, suggesting that the space group was indeed $P\bar{3}$ and not $P3$ [4]. The results obtained for $P\bar{3}$ space group (see Table 1) show that the deviations from the positions in the parent B2 structure are 0.031c for Ti2(z) and 0.009c for Ti3(z); while that for Ni2(z) and Ni3(z) are 0.065c and 0.021c, respectively. Whereas the Ti3(z) and Ni3(z) stay at approximately the same z-positions as those in the B2 parent phase, the shift values for both Ti3(x,y) and Ni3(x,y) are very small. The present results show that the structure is centrosymmetric with the symmetry centre located at Ti1(x,y,z) and Ni1(x,y,z).

References

- [1] Sitepu, H., Schmahl, W. W., Khalil Allafi, J., Eggeler, G., Dlouhy, A., Toebbens, D.M. and Tovar, M. (2002a). *Scripta Materialia*, **46**, 543-548.
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- [3] Sitepu H, O'Connor, B.H. and Li, D.Y. (2005). *J. Appl. Cryst.* **38**, In print.
- [4] Sitepu, H. (2003). *Textures and Microstructures*. **35**, 185-195.