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Crystal structure of three Ni-Mn-Ga alloys in powder and bulk materials

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Abstract. In NiMnGa alloy the crystal structure of low temperature phase is strongly related to transformation temperature. In the present study three NiMnGa alloys with different transformation temperatures were studied. Alloy A has the martensitic start temperature (M_s) near ambient temperature and M_s of Alloy B is near Curie point (T_C) whereas M_s of Alloy C M_s is well above T_C . The crystal structures of three alloys were studied by X-ray diffraction in powder and bulk materials. The low temperature phase of single crystal in Alloy A was tetragonal phase with $c < a$, in Alloy B it was mixture of orthorhombic phase and tetragonal phase with $c > a$, and in Alloy C such a phase was tetragonal phase with $c > a$. The crystal structure of Alloy A in bulk material is in good agreement with powder diffraction, but in Alloys B and C there is a lack of conformity between bulk and powder. Furthermore, the difference of crystal structure in powder and bulk is discussed in more detail.

1. INTRODUCTION

NiMnGa alloys have been attracting intensive attention in recent years due to a giant magnetic induced strain. In this alloy system the high temperature cubic phase was found to be $L2_1$ ordered structure [1]. The structure of low temperature phase is both composition and transformation temperature dependent. Tetragonal phase with 5-layered modulation was determined by X-ray diffraction in single crystal [2]. Non-layered tetragonal phase with $c > a$ was discovered with X-ray powder diffraction in [3, 4]. Recently 7-layered and 10-layered modulated orthorhombic phases were analyzed by TEM using periodic stacking fault approach [5]. In this same study, a certain unconformity existed with structures of bulk and ribbon materials. However, in the present work the crystal structures of powder and bulk materials were studied, where a good agreement was obtained with 5-layered martensitic materials.

2. EXPERIMENTAL

Alloys A and B were manufactured using induction melting and casting into precision ceramic moulds in argon atmosphere and following solidification at the rate of 0.5 mm/min in the Bridgman-type crystal growth furnace in AdaptaMat Ltd. Alloy C was produced at Outokumpu Research Oy. All three alloys were homogenized at 1273 K for 72 h, and thereafter annealed at 1073 K for 48 h in vacuum quartz ampoule after cutting. The material for powder samples was cut from annealed ingots by sparkle saw and cracked into small particles by iron ball milling in argon atmosphere. Powder samples were further annealed at 1073 K for 96 h in vacuum quartz ampoule. Ball milling of Alloy A took approximately 30 min, of Alloy B for 2 hours and of Alloy C for approximately 6 hours. Particle size was selected by using 75 μm sieve. The average particle size was measured in SEM SEI (secondary electrons image) by image analysis program and it was confirmed to be approximately 30 μm . The transformation temperatures were determined both by differential scanning calorimeter (DSC) and by magnetic susceptibility measurements by using heating-cooling rate of 2 K/min. The powder diffraction was measured by Philips diffractometer PW1710 with $\text{Cu-K}\alpha$ radiation and the single crystal X-ray diffraction by Philips X'pert-MRD with $\text{Co-K}\alpha$ radiation. Both diffractometers were equipped with laboratory-made heating cooling stage applying

Peltier-element heater. The K_{β} radiation was removed by graphite monochromator attached to the detector of PW1710. The powder diffraction measurements were made at step size of $0.01^{\circ}/\text{step}$, $15 \text{ s}/\text{step}$ having divergent slit 1° and receiving slit 0.1 mm . The diffractometer was calibrated with Si-powder standard sample. The beam size of X-ray was approximately around 3 mm in X'pert-MRD. The alloy compositions for both powder and bulk samples were determined with EDS method in LEO-1450 SEM. Lattice parameters were determined by using Rietveld refinement program, LHPM-Reitica.

3. RESULTS AND DISCUSSION

The compositions and transformation temperatures of all alloys for both powder and bulk materials are listed in Table 1. Alloy A has martensitic transformation just above room temperature (RT). This alloy shows approximately 6 % magnetic field induced stain. Two kinds of martensite were simultaneously formed during martensitic transformation which was just below T_C in Alloy B. One was orthorhombic phase with 7-layered modulation and the other was non-layered tetragonal phase with $c > a$. During further cooling the most of orthorhombic phase transformed into non-layered tetragonal phase due to inter-martensitic transformation which occurred at 284 K . The compositions and transformation temperatures in powder and bulk coincide with each other in Alloys A and B. However transformation temperatures remarkably decrease in powders of Alloy C. Additionally, 1.4 at% Fe was found only in powder of Alloy C which might have mixed into the powder from the steel balls during the exceptionally long ball milling procedure of this particular alloy.

Table 1. Compositions and phase transformation temperatures.

Alloy		Composition (at%)				Transformation temperature (K)				
		Ni	Mn	Ga	Fe	M_s	M_f	A_s	A_f	T_c
A	Bulk	49.5	28.6	21.9		305.8	299.8	314.4	318.8	376
	Powder	49.4	28.8	21.8		305	300.1	312.9	319.8	368
B	Bulk	48.4	31.3	20.3		354	347.4	356	363.2	363
	Powder	48.4	31.8	19.8		354.2	346.5	354.1	360.6	362
C	Bulk	52.6	26.7	20.7		465	459	468	476	371
	Powder	52.2	25.6	20.8	1.4	423	383	393	428	352

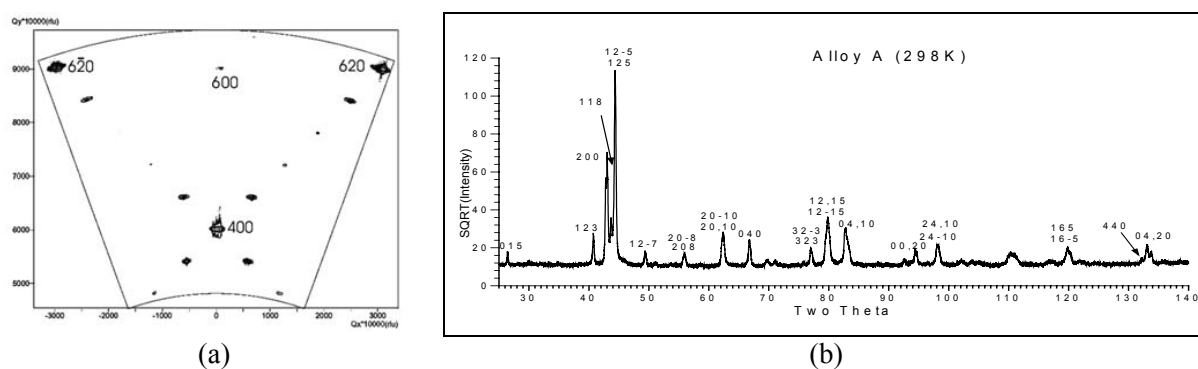


Figure 1. (a) The X-ray intensity distribution in the plane of reciprocal space showing extra spots connected with 5-layered modulation structure of Alloy A; (b) Powder diffraction pattern of martensite in Alloy A.

The martensite structure of Alloy A is a 5-layered martensite which was confirmed both by powder diffraction and single crystal X-ray diffraction. Single crystal sample was elaborately prepared for X-ray diffraction which revealed that it was nearly in single martensitic variant state. The single variant sample shows no contrast under optical microscope. Furthermore texture measurement confirmed that no second twin variant existed. However, extra spots were found in reciprocal direction $\langle 110 \rangle^*$, shown in Fig. 1(a), which equally divided the distance between main spot into 5 parts as the same as in reference [2]. Here, the index refers to pseudo-cubic axes. The intensity ratio of basic spot and the first strong extra spot was approximately 10. Powder diffraction pattern of martensite in Alloy A is shown in Fig. 1(b). In this case,

the index refers to the monoclinic axes. Modulation model was used for structure analysis, and coefficients of displacement wave from reference [2] were applied to Alloy A. It was found that the space group P2/m is the best fit for the supposed model. The lattice parameters of Alloy A and the weight profile values (R_{wp}) obtained from Rietveld refinement are listed in Table 2. The lattice parameters referring to the pseudo-cubic axes are also given in Table 2 for comparison.

Table 2. Lattice parameters of studied alloys at different temperatures.

Alloy	Phase (measuring temperature)	Obtained from powder (nm)							Obtained from bulk (nm)				
		Lattice	<i>a</i>	<i>b</i>	<i>c</i>	β	γ	Space Group	R_{wp} -value	<i>a</i> (± 0.001)	<i>b</i> (± 0.001)	<i>c</i> (± 0.001)	γ (± 0.5)
A	Austenite (324K)	Cubic	0.5837					Fm-3m	18.65				
	Martensite (RT)	Monoclinic	0.4219	0.5600	2.0977	90.2		P2/m	13.56				
		Pseudo-cubic	0.596	0.594	0.560		90.3			0.595	0.595	0.561	90
B	Austenite (391K)	Cubic	0.5850					Fm-3m	19.32				
	Orthorhombic phase (RT)	Monoclinic	0.4273	0.5529	2.9606	93.2		P2/m					
		Pseudo-cubic	0.618	0.584	0.553		89.4			0.621	0.580	0.550	90
	Tetragonal phase (RT)	Undetermined in powder diffraction									0.550	0.550	0.657
C	Martensite(RT)	Monoclinic	0.4253	0.5459	2.9440	93.8		P2/m					
		Pseudo-cubic	0.618	0.578	0.546		89.4			0.544	0.544	0.664	90

According to powder diffraction, the shuffling system of modulation structure is $(110)[\bar{1}\bar{1}0]$ referring to pseudo-cubic axes. In single crystal diffraction the extra spots were occurring at both $[\bar{1}\bar{1}0]^*$ and $[110]^*$ directions in Fig. 1(a). The intensity of each extra spot in direction $[110]^*$ is twice as high as one in $[\bar{1}\bar{1}0]^*$. In order to explain such a behavior, there can be two possible reasons. At first, there may exist different domains whose shuffling systems are $(110)[\bar{1}\bar{1}0]$ and $(\bar{1}\bar{1}0)[110]$ separately, but their orientation are the same from the point of view of pseudo-cubic axes. Second possibility suggests that the modulation of lattice is more complex.

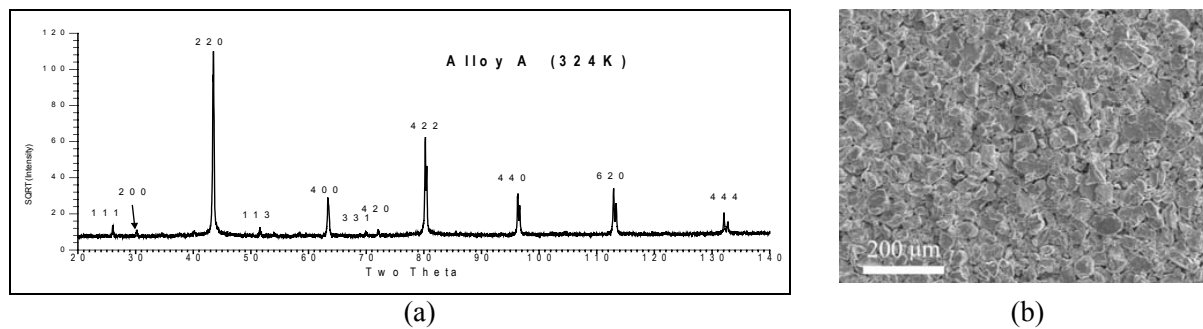


Figure 2. (a) Austenite powder diffraction of Alloy A; (b) SEM SEI image of powder sample of Alloy A.

The powder diffractions of high temperature phase were measured at different temperatures for Alloys A and B. The observed reflections show both the first and the second neighbor ordering, providing austenite structure to be a $L2_1$ ordered lattice. One of austenite powder diffraction pattern measured at 324 K is shown in Fig. 2(a). The morphology of Alloy A powder is shown in Fig. 2(b) where one can discover the average particle size. The thermal expansion coefficient was estimated to be $17.7 \times 10^{-6} \text{ K}^{-1}$ in Alloy A by measuring changes of lattice parameter *a* with temperature. In all the powder diffraction spectra the trace of first three strong lines of MnO were visible. Lattice parameters of cubic phase were shown in Table 2. Fig. 3 shows powder diffractions of experimental measurements and calculations. Single crystal X-ray diffractions revealed that the low temperature phase in Alloy B was a mixture of two kinds of martensite: one is orthorhombic phase with 7-layered modulation and the other is non-layered tetragonal phase with $c > a$. Powder diffraction confirmed the existence of 7-layered martensite but the other phase remained undetermined. 7-layered martensite was analyzed by using modulation model from reference [2]. It was found that the main reflections fit the 7-layered model very well but the additional reflections from

modulation slightly deflect from the calculated one. In Alloy C where martensitic transformation temperature is much higher than Curie point, non-layered tetragonal phase is formed during martensitic transformation. However, powder diffractions of Alloy C indicated a 7-layered martensite structure with a slight deflection of modulation peaks. The deflection of modulation peaks might suggest that the 7-layered martensite is an incommensurate modulated structure. The lattice parameters of Alloy B and C are given in Table 2. Because the average particle size used for powder diffraction in all three alloys was the same, one possible reason for the different crystal structures in powder and bulk in Alloys B and C might be due to the deformation during ball milling even though all the alloys were annealed afterwards. The difference in the preparation procedure can be explained by the different mechanical properties of the alloy as the high temperature alloys tend to have better strength properties [6].

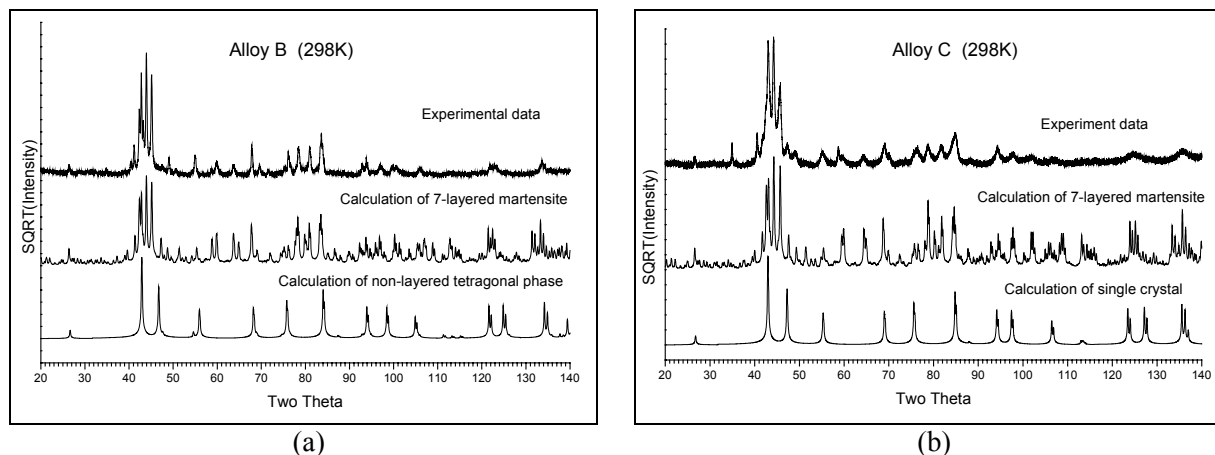


Figure 3. Powder diffraction patterns from experimental and calculation in Alloy B (a) and in Alloy C (b).

4. CONCLUSIONS

Three NiMnGa alloys were studied by X-ray diffraction in powder and bulk material. In Alloy A there exists good agreement in powder diffraction and single crystal X-ray diffraction. Martensitic structure of Alloy A was a 5-layered modulated lattice, and lattice parameter was determined by Rietveld refinement. In Alloys B and C the powder diffraction patterns did not correspond with the crystal structure in bulk material.

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References

- [1] Webster P.J., Ziebeck K.R.A., Town S.L and Peak S.M., *Phil. Mag. B* **49** (1984) 295-310
- [2] Martynov, V. V. and Kokorin, V. V., *J. Phys. III France*, **2** (1992) 739-749.
- [3] Wirth S., Leithe-Jasper A., Vasi'ev A.N., Coey J.M.D., *J. Magn. Magn. Mater.* **167** (1997) L7-L11
- [4] Wedel B., Suzuki M., Murakami Y., Wedel C., Suzuki T., Shindo D., Itagaki K., *J. Alloys Comp.* **290** (1999) 137-143.
- [5] Pons J., Cherneko V.A., Santamarta R. and Cesari E., *Acta. Mater.* **48** (2000) 3027-3038.
- [6] Koho K, Vimpari J., Straka L., Lanska N. Söderberg O, Ullakko K., and Lindroos V. K., "Behaviour of NiMnGa Alloys Under Mechanical Stress", ICOMAT02 Helsinki, Finland, June 10-14, 2002