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STRUCTURE ANALYSIS OF NiAl MARTENSITE

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ABSTRACT

Neutron elastic scattering experiments were performed in order to investigate the structure of the low temperature martensitic phase of $Ni_{62.5}Al_{37.5}$ alloy. The average structure analyzed from the integrated intensity was approximately described by the (5,-2) structure proposed by Martynov et al. Small deviation from the exact (5,-2) model in the positional parameters and the anomalously large Debye-Waller factor were obtained. The observed satellite profiles show asymmetrical broadening, and the peak positions shift from the regular reciprocal lattice points. These anomalous features of scattering profiles were tentatively interpreted by introducing spatial modulation of the strain and order parameters.

1. INTRODUCTION

The mechanism of martensitic transformations in metal alloys has been investigated in recent years specially in connection with the precursor phenomena and phonon instability. The transformation of Ni_xAl_{1-x} alloys($0.60<x<0.64$) from a β_2 phase to a 7M low temperature phase* is one of the typical example[1-6]. Shapiro et al.[3,4] extensively studied the [110] TA phonon mode of Ni-Al alloys by neutron inelastic scattering, and found the existence of a pronounced dip whose position in q space was composition dependent. In the same q range, elastic diffuse scattering also appeared which corresponded to the tweed strain image[5] in the electron microscope. When the composition x was 0.625, the phonon

* In the literature, the seven layered phase of Ni-Al alloys is conventionally described as 7R martensite. Since the symmetry of the martensite lattice is monoclinic instead of rhombohedral, we use the expression "7M martensite" here after.

dispersion curve showed a marked, but incomplete, softening at $q \sim 1/6$, instead of $q \sim 1/7$.

The structure of the seven layered martensite of Ni-Al alloy was firstly studied by Martynov et al.[6] They made an x-ray diffraction experiment of the 7M phase which was induced by the external tension at room temperature; 4.5% elongation along the $[110]_\beta$ direction. The diffraction pattern was compared with model structures which were constructed by the seven layered stacking sequence of $(110)_\beta$ planes. The (5,-2) sequence gave the best consistency to the experimental results. However, the precise structure of the low temperature 7M martensite in Ni-Al alloy is unknown so far. Furthermore, the transition scheme to construct the 7M structure is still unclear. The purpose of the present paper is to study the structure of the 7M martensite more precisely in connection with the transformation mechanism.

2. EXPERIMENTAL AND ANALYSES

The neutron diffraction experiments were performed at the Brookhaven National Laboratory's High Flux Beam Reactor. The sample of $Ni_{62.5}Al_{37.5}$ was a single crystal which was the same one used in the previous experiments[4,7,8]. It was glued on an aluminum rod and installed in a sealed Al can filled with He gas. Data were collected at 15K, far below the transition temperature(T_M=80K). The structure of the β_2 phase is a CsCl type having a lattice parameter of a_0=0.2858 nm at room temperature. When the temperature was cooled down from the room temperature, the domain structure appeared at T_M so that the main Bragg spot in β_2 phase split to several Bragg spots. After careful survey of the reciprocal lattice, we could separate the scattering plane of the low temperature phase associated with few domains into independent lattice frame.

2.1 Unit cell and strain

Satellite peaks characterizing the 7M martensite structure were observed along $\langle 110 \rangle_\beta$ directions. The position of these peaks was almost, but not exactly, $q=1/7$, and the spacing was non-uniform. The line shape of the peaks was anomalously elongating along the direction of the modulation vector. Some of them had a shoulder peak and seemed to be composed to two peaks. The unit cell of the 7M martensite was determined with the averaged peak positions to be monoclinic cell. Obtained cell parameters with $(2\ 0\ 6)_m$, $(0\ 2\ 0)_m$ and $(2\ 0\ \bar{8})_m$ Bragg points are a_m=0.4172 nm, b_m=0.2690 nm, c_m=1.4450 nm and β_m=94.37° at 15K. These values are in excellent agreement with those given by Martynov et al.[6] for 7M martensite in tension. The relation ship between the parent cubic cell and the 7M cell in the reciprocal lattice is the following:

$$a_m^* = 1/7[\,4\ \bar{3}\ \ 0]_c\ ,$$
$$b_m^* = [\,0\ \ 0\ \bar{1}]_c\ ,$$
$$c_m^* = 1/7[\,1\ \ 1\ \ 0]_c\ .$$

Schematic reciprocal lattice is already given in figure 3 of ref.4. Therefore, the Bragg peak $(100)_c$ turns to $(1\ 0\ 3)_m$, $(1\ 0\ \bar{4})_m$ and $(0\ 1\ 0)_m$ Bragg points.

The strain at the martensitic transformation is easily calculated from the above relationships and the obtained lattice parameters:

$$e_{xx}=-0.004,$$
$$e_{yy}=0.058,$$
$$e_{zz}=-0.052.$$

These value seems to be expressed as

$$\varepsilon=0.078(e_{yy}-e_{zz})/\sqrt{2},$$

and is comparable with Martynov's experiment. However,it is suitable to introduce the alternative set of shear strains

$$\varepsilon=-0.044\,\varepsilon_2+0.065\,\varepsilon_3,$$

where

$$\varepsilon_2=(e_{xx}-e_{yy})/\sqrt{2},$$
$$\varepsilon_3=(e_{xx}+e_{yy}-2e_{zz})/\sqrt{6},$$

when we combine the direction of the modulation wave and the obtained strains. Here, the modulation vector is chosen along $[110]_c$ direction following ref. 4. In any case, the distortion is shear strain and hence there is almost no volume change at the martensitic transformation.

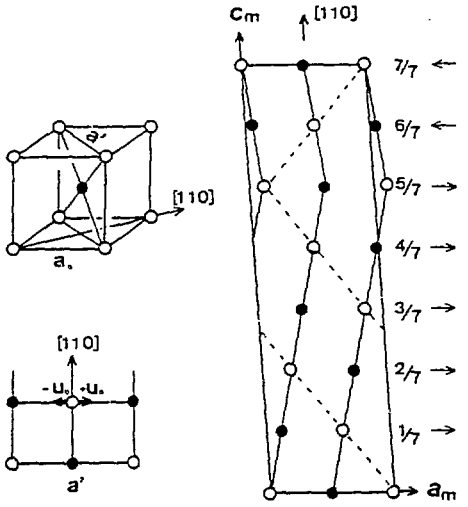

Figure 1. (5,-2) stacking seaquence model.

2.2 (5,-2) model and the averaged structure of 7M martensite.

Let us consider how the (5,-2) structure is constructed . As shown in figure 1, the (110) plane of the CsCl type structure is treated as a basal plane of the stacking sequence propagating to the [110] direction. Each (110) plane shifts to plus or minus direction; $+u_0$ or $-u_0$. Here a' denotes the length of the plane $\sqrt{2}a_0$ and turns to be a_m. When the stacking sequence of the seven layered structure is given by $+N_1u_0$ and $-N_2u_0$ ($N_1+N_2=7$), we obtain the (N_1,-N_2) model. Shown in figure 1 is the (5,-2) structure whose unit cell is monoclinic, and the monoclinic angle β_m is calculated as

$$\beta_m=90+\tan^{-1}(a'-2(N_1-N_2)u_0)/(N_1+N_2)a'.$$

Martynov et al. assumed the shift of each plane as $u_0=a'/12$ to adjust the experimental results. Calculated β_m is 94.1° .

Following, we consider the average structure of the 7M martensite since the position of the satellite reflection does not form the regular reciprocal lattice. We limited the collection of the Bragg intensity into the $(H\ 0\ L)_m$ reciprocal plane, hence the structural analyses is also limited to the $(x\ 0\ z)_m$ plane. We simply assumed that the feature of the basal plane is maintained except the uniform distortion of the plane. The collection of the Bragg intensity was performed for $1\leqq H_m\leqq 4$ and $-13\leqq L_m\leqq 9$. As the initial step of the structural analysis of 7M martensite, we used the exact (5,-2) model with $u_0=a_m/12$. This model automatically gives the positional parameters of each atoms in the basal plane so that we have no adjustable parameters except the Debye-Waller factors.

The positional parameters of Al atoms $(x\ 0\ z)_m$ are tabulated in Table 1. These positional parameters are identical with those given by Martynov et al. The position of Ni atoms is $(x+1/2\ 1/2\ z)_m$ in each layer. The least square fitting procedure of the conventional structural analyses was applied to minimize

$$R2=(\text{scale}\cdot |F_{ob}| - |F_{cal}|)^2,$$

where F denotes the structure factor. The scattering amplitudes of Ni and Al atoms in $Ni_{62.5}Al_{37.5}$ are $b_{Ni}=10.3$ and $b_{Al}=5.7$. The total number of the used data F_{ob} is 71 and the adjustable parameters in exact (5,-2) model are four, including the scale factor. We assumed that the Debye-Waller factors of each atoms are the same. Obtained U parameters (Debye-Waller factor) are given in the table. The final R-factor is 13.7% and the agreement seems satisfactory.

	Exact (5,-2) model				Extended (5,-2) model				
z	x	U_{11}	U_{13}	U_{33}	x	U_{11}	U_{13}	U_{33}	δx
0	0	4.42(1)	-0.29(2)	2.85(2)	0	4.21(1)	-0.34(1)	2.59(2)	0
1/7	26/42	-	-	-	25.706/42	2.62(1)	-	-	-0.0070(1)
2/7	10/42	-	-	-	10.074/42	4.67(2)	-	-	+0.0018(1)
3/7	36/42	-	-	-	36.190/42	5.25(3)	-	-	+0.0045(1)
4/7	20/42	-	-	-	20.117/42	6.93(4)	-	-	+0.0028(1)
5/7	4/42	-	-	-	3.347/42	3.54(2)	-	-	-0.0155(1)
6/7	23/42	-	-	-	22.510/42	3.19(2)	-	-	-0.0117(1)
		R=13.7%				R= 9.5%			

Table 1. Positional and U parameters of Al atoms. Position of Ni atoms are assumed to be $(x+1/2\ 1/2\ z)_m$. The unit of U_{ij} is 10^{-4} nm^2 ,and the mean amplitude is given by $\sqrt{U_{ij}}$.

We extended the (5,-2) model to the general stacking sequence model where the positional parameters x are treated as adjustable parameters. Simultaneously, U_{11} parameters are treated independently for each layers. Note that this treatment gives the general stacking sequence, and the (5,-2) sequence is included as the special case. The obtained parameters are given in the table. As tabulated in the table, obtained positional parameters are very close to the exact (5,-2) model, and seems to be the modified (5,-2) sequence. The deviation δx from the ideal position is given at the last column, and the maximum deviation is $\delta x \cdot a_m \sim 0.005$ nm. On the other hand, the obtained U_{11} parameter gives the mean amplitude of the basal plane along a_m direction as $\langle u_x \rangle \sim 0.02$ nm, one magnitude larger than the above deviation. The final R-factor drops to 9.5%.

2.3 Peak shift of satellite reflections

As mentioned in the previous section, the position of the satellite peaks was not exactly 1=1/7. From the scattering profiles along $[H\ 0\ \xi]_m$ direction, we

obtained the shift of the peak position Δ from the regular monoclinic reciprocal lattice point as $[H\ 0\ L+\Delta]_m$. In figure 2, observed shifts are shown as a function of indices $(H\ 0\ L)_m$ by open and solid circles. Solid circles denote the satellite positions where there are corresponding cubic lattice points. For instance, $(2\ 0\ 6)_m$ and $(2\ 0\ -8)_m$ Bragg points are corresponding to $(0\ 2\ 0)_c$ and $(2\ 0\ 0)_c$ points respectively. When the profile has a shoulder peak, the position of the minor peak is plotted by a triangle mark. As is shown in the figure, the reciprocal points expressed by solid circles seem to maintain the regular monoclinic lattice, while other Bragg points deviate from the lattice point into the direction of negative Δ-values. There is a systematic oscillation of seven period. Furthermore, the average deviation increases as H_m is increased.

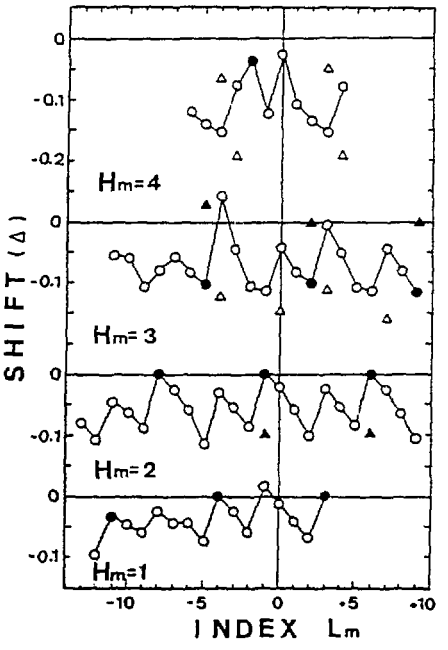

Figure 2. Observed peak shift Δ.

Part of the anomalous features of shift pattern in figure 2 may be understood by considering that there is coexistence of two different monoclinic lattices characterized by β_m=94.37° and β'_m=93.82° . The reciprocal lattice points of the latter (with β'_m) shift to the -c* direction from those of the former.

3. DISCUSSION

We have observed complicated shifts and anomalous broadening of satellite reflections of 7M martensite, and partly interpreted by the coexistence of the two different monoclinic lattices. In this section, we give a tentative interpretation of the physical origin of these complicated features.

The atomic positions x_n of the averaged (5,-2) structure given in the previous section would be analyzed into Fourier components as follows;

$$x_n = x_n^0 + \varepsilon \cdot a \cdot n + \sum_{m=1}^{3} (\xi_m \cdot e^{2\pi i (m/7) n} + C.C) ,$$

where x_n^0 is the atomic position of the original cubic structure. We consider that both the bulk strain ε and ξ_m's are allowed to be spatially modulated, and express the r dependence explicitly as $\varepsilon(r)$ and $\xi(r)_m(r)=A_m(r)\cdot e^{i\phi_m(r)}$. (Note ξ_m is a complex order parameter.) Recently, Barsch and Krumhansl[9] pointed out that at a first order phase transition, there may appear a metastable phase where the order parameter is spatially modulated taking on two discrete values alterna-

tively with a period of mesoscopic size (a crest riding periodon). The observed coexistence of the two monoclinic lattices with different monoclinicity may be interpreted in terms of this 'periodon' picture*. Due to the coupling between ξ_m's and ε, we have[10]

$$A_1^2(r) \cdot A_2(r) \propto \varepsilon(r).$$

Physically, this means that the internal distortions $\xi_m(r)$ are preferentially embedded on the strongly strained part of the crystal. The corresponding diffraction effect would be that the satellite reflections tend to shift towards the fictitious lattice points of the more strongly strained lattice[11]. This is consistent with the observed behavior that the averaged shift increase with increasing of H_m. Further details of the shift pattern should depend on the phase modulation $\phi_m(r)$, which has been neglected in the present discussion. Detailed analysis including $\phi_m(r)$ is left as a future problem.

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*Recently, Seto et al.[12] also observed the coexistence of two tetragonal lattices with different tetragonality at the fcc-fct martensitic transformation of Fe-Pd alloy.

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