Site Determination of Third Elements in TiAl Compound by X-ray Diffractometry*

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The X-ray diffraction method to determine the long range order parameter in binary alloys has been extended to examine the site occupancy of third elements (V, Mn, Zr and Nb) and the amount of mutually exchanged Ti and Al atoms in TiAl-phase for ternary TiAl-X alloys.

In the present analysis, unknown parameters β_{Al} and β_X were determined by solving simultaneous equations $\beta_{Al} = P + Q \times \beta_X$ with respect to different P and Q values, where β_{Al} or β_X represents the amounts of Al or X occupied in the Al site in TiAl-phase, and P and Q are experimentally determined; the former depends predominantly on the ratio of integrated intensity whereas the latter only depends on the atomic scattering factors in superlattice reflections.

It turned out that V and Mn atoms occupy predominantly the Al site whereas Zr and Nb atoms occupy the Ti site; the amount of mutually exchanged Al and Ti atoms decreases with increasing concentration of V and Mn, whereas it decreases at first and then increases for the concentration above 5 at% of Zr and Nb.

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I. Introduction

Recently, intermetallic compounds such as Ni_3Al , TiAl, NiTi and FeSi₂ have widely been used as heat-resistant and functional materials; attempts are made to improve the mechanical properties of these compounds by addition of various third elements. In order to understand the mechanism for the improvement of the mechanical properties, it is required to reveal the occupation sites of additional elements and the mutual exchange behavior of the constituents when various third elements are added into these compounds.

In the present study, we propose a new X-ray analytical method for determining the occupation sites of additional elements, and we also report on the mutual exchange behavior of Ti and Al when various third elements are added into TiAl.

To date, the occupation sites of additional elements in compounds, e.g. Ni_3Al , have been determined by the following methods;

- (1) extension of a single-phase region in ternary phase diagrams⁽¹⁾⁽²⁾
- (2) thermodynamics⁽²⁾
- (3) X-ray diffractometry⁽³⁾⁽⁴⁾
- (4) ALCHEMI (Atom Location by Channelling Enhanced Microanalysis)⁽⁵⁾⁻⁽⁷⁾
- (5) Mössbauer effect⁽⁸⁾
- (6) FIM (Field Ion Microscope)⁽⁹⁾⁽¹⁰⁾
- (7) PAC (Perturbed Angular Correlation)⁽¹¹⁾

(8) Ion Channelling⁽¹²⁾

(9) RBS (Rutherford Backscattering)⁽¹²⁾

Among these, the methods (3)–(9) are directly associated with experiments, whereas (1) and (2) are indirect. The method (3) or (4) uses a conventional X-ray apparatus or electron microscope, while rather special equipments are used in (5)–(9). The method (6) is considered to be the most direct for determining the occupation sites of third elements in the compounds. However, this gives rise to results⁽⁹⁾⁽¹⁰⁾ in contradiction to those determined by (7)⁽¹¹⁾ or (9)⁽¹²⁾, concerning the occupation sites of Hf in Ni_3Al .

Ochiai *et al.*⁽²⁾ have shown that the method (1) or (2) can determine the occupation sites of X in Ni_3Al -X (X=Mn, Ti, Nb etc.). The occupation sites of X have been quantitatively determined by X-ray diffractometry for Ni_3Fe -X⁽⁴⁾, and by ALCHEMI for TiAl-Nb⁽⁶⁾ and CuAu-Pd⁽⁷⁾. Some other studies by (3) or (4) have provided only qualitative information concerning the occupation sites of the third elements.

Our method proposed here utilizes the difference in the reflection-angle dependence of the atomic scattering factors of alloy constituents; this can quantitatively determine the occupation sites of elements without using AXS (Anomalous X-ray Scattering) technique. This method will be compared with (3) or (4) in §IV. In the present study, TiAl alloys with several third elements are analysed by this method.

The intermetallic compound TiAl has the $L1_0$ -type crystal structure, and it is constructed by alternately stacking the (001) and (002) planes with Ti and Al atoms (Fig. 1); the coordinates of each atom species are as follows; (0, 0, 0) and (1/2, 1/2, 0) for Ti atoms (α -site), and (1/2, 0, 1/2) and (0, 1/2, 1/2) for Al atoms

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Fig. 1 $L1_0$ structure of TiAl superlattice.

(β -site). When third elements are dissolved in TiAl, they can substitute for Ti or Al atoms. Since the alloys consisting of two phases, TiAl (major) and Ti_3Al (minor), are most ductile, we pay attention to the TiAl-phase in this duplex-phase structure dissolving third elements such as V, Mn, Zr and Nb (2.5–5at%).

II. Experimental Procedures

1. Sample preparation

TiAl-base alloys with various additional elements were prepared by arc-melting Al(99.99%), Ti(99.8%), Zr(99.8%), V(99.8%), Mn(99.8%) and Nb(99.9%) under an argon atmosphere; they were remelted three times to ensure their homogeneity. The atomic ratio of Ti to Al was fixed to 52.2 : 47.8 (Ti-enriched beyond the stoichiometric composition). For further homogenization, these alloys were vacuum sealed in quartz tubes with a pressure lower than 6.7×10^{-3} Pa, annealed for 691 Ks at 1273 K and then water-quenched.

The samples were polished with emery papers and then buffed for analysis of the chemical compositions. Powdered samples crushed below 300 mesh were used for X-ray diffractometry; prior to measurements, they were annealed in vacuum at 1273 K for 600 s to eliminate strains.

2. Analysis of chemical composition

The chemical composition of the TiAl-phase was determined as follows by using a scanning electron microscope equipped with an energy dispersive X-ray analyzer (EDAX-9100). The X-ray microprobe intensity spectra were measured three times each for 150 s on different areas (3 mm $\times$ 3 mm) of each bulk sample; we regarded a representative spectrum that corresponded the average of the three measurements as a standard. Then, we could obtain a relationship between the nominal composition and intensity for the standard spectrum. Based on this relationship, the chemical composition of the

TiAl-phase was determined; at least nine measurements were made taking care of avoiding the Ti_3Al -phase that should give a higher Ti concentration.

3. X-ray diffractometry

X-ray diffraction patterns were measured on powdered samples using a diffractometer with CuK_α radiation at 40 KV and 30 mA. Each powdered sample was packed into a sample holder to ensure that the surface of the sample (15 mm $\times$ 20 mm $\times$ 0.5 mm) is flat. The integrated intensities for the superlattice reflections (001), (110) and (201) and the fundamental reflection (222) in TiAl were determined with a scintillation counter at room temperature. Figure 2 shows the X-ray diffraction pattern for Ti-47.8 at%Al alloy. In the intensity measurements, we took account of the effects of preferred orientation in the powdered samples and an overlap of reflections. The intensity measured while a sample was spinning revealed no serious preferred orientation in case the sample had been crushed below 300 mesh. Figure 2 indicates that the weak reflection (004) due to Ti_3Al (α_2) overlaps the skirts of the reflection (222) due to TiAl. However, the overlapping part of the reflection (004) was subtracted by comparing the intensities of the reflection (201) due to the Ti_3Al -phase in the samples with those of the reflections (004) and (201) in the Ti_3Al single phase. We did not use the reflections (111), (200) and (002) in TiAl in our analysis, because (111) in TiAl and (002) in Ti_3Al overlap, and (200) and (002) in TiAl also overlap when the axial ratio $c/a \approx 1$. The intensity measurements were repeated ten times for each reflection, in order to minimize statistical errors.

III. Details of Analysis

First of all, we assume that the A atom (Ti) and B atom

Fig. 2 X-ray diffraction pattern for Ti-47.8 at%Al alloy composed of TiAl(γ) and $Ti_3Al(\alpha_2-D0_{19})$ phases.

(Al) predominantly occupy the α -site and the β -site in TiAl, respectively. Furthermore, we define the fraction of A_j atom ($A_1=A$, $A_2=B$, $A_3=X$) in each site as α_j or β_j and the atomic scattering factor of A_j atom as $f_{A_j}(\theta)$. Using these definitions, the total atomic scattering factor, $f\alpha$ or $f\beta$, for each site is given by;

$$\left. \begin{aligned} f\alpha &= \sum_j f_{A_j}(\theta) \times \alpha_j \\ f\beta &= \sum_j f_{A_j}(\theta) \times \beta_j \end{aligned} \right\} \quad (1)$$

It is well established that the scattering intensity, I_r , for the reflection (h_r, k_r, l_r) is given by;

$$I_r = K \times m(r) \times T(\theta_r) \times L(\theta_r) \times |F(h_r, k_r, l_r)|^2,$$

where $m(r)$ is the multiplicity factor, $T(\theta_r)$ the temperature factor, $L(\theta_r)$ the Lorentz polarization factor and $F(h_r, k_r, l_r)$ the structure factor; K is a constant irrespective of diffraction angles. Absorption factor is not included because our samples are planes thicker than 0.3 mm.

Thus, the integrated intensity ratio of the superlattice reflection to fundamental reflection, $H(=I_s/I_f)$, is given by

$$H = \frac{m(s)}{m(f)} \times \frac{T(\theta_s)}{T(\theta_f)} \times \frac{L(\theta_s)}{L(\theta_f)} \times \frac{|F(h_s, k_s, l_s)|^2}{|F(h_f, k_f, l_f)|^2} \quad (2)$$

On the other hand, the structure factors of the superlattice and fundamental reflections in TiAl are given by

$$\left. \begin{aligned} F(h_s, k_s, l_s) &= 2|f\alpha - f\beta| \\ F(h_f, k_f, l_f) &= 2|f\alpha + f\beta| \end{aligned} \right\} \quad (3)$$

When we define the amount of Ti, Al and a third element X that occupy $\alpha(\beta)$ site as $\alpha_{Ti}(\beta_{Ti})$, $\alpha_{Al}(\beta_{Al})$ and $\alpha_X(\beta_X)$, we obtain the following relations between these six unknown parameters and the compositions of Ti, Al and X, i.e. C_{Ti} , C_{Al} and C_X , in the TiAl-phase:

$$\left. \begin{aligned} \alpha_{Ti} + \beta_{Ti} &= C_{Ti} \\ \alpha_{Al} + \beta_{Al} &= C_{Al} \\ \alpha_X + \beta_X &= C_X \end{aligned} \right\} \quad (4)$$

$$\left. \begin{aligned} \alpha_{Ti} + \alpha_{Al} + \alpha_X &= 0.5 \\ \beta_{Ti} + \beta_{Al} + \beta_X &= 0.5 \end{aligned} \right\} \quad (5)$$

We should notice that there are only two independent parameters, β_{Al} and β_X , in eqs. (4) and (5); they can be determined as follows. We assume that the α -site and β -site are principally occupied by Ti and Al atoms, respectively. Inserting eqs. (1), (3), (4) and (5) to eq. (2) leads to

$$\beta_{Al} = \frac{1}{2\{f_{Ti}(\theta_s) - f_{Al}(\theta_s)\}} \times \left[\left\{ \frac{H}{m \times T \times L} \right\}^{1/2} \times F'_f - F'_s \right] + Q \times \beta_X, \quad (6)$$

where

$$m = m(s)/m(f), \quad T = T(\theta_s)/T(\theta_f), \quad L = L(\theta_s)/L(\theta_f)$$

$$F'_f = f_{Ti}(\theta_f) \times C_{Ti} + f_{Al}(\theta_f) \times C_{Al} + f_X(\theta_f) \times C_X$$

$$F'_s = f_{Ti}(\theta_s) \times (C_{Ti} - 1) + f_{Al}(\theta_s) \times C_{Al} + f_X(\theta_s) \times C_X,$$

and

$$Q = \frac{f_X(\theta_s) - f_{Ti}(\theta_s)}{f_{Ti}(\theta_s) - f_{Al}(\theta_s)}. \quad (6')$$

Equation (6) is further simplified as

$$\beta_{Al} = P + Q \times \beta_X. \quad (7)$$

We should notice that eq. (7) is a linear equation with respect to β_{Al} and β_X , since P and Q involving H , C_{Ti} , C_{Al} and C_X are already known. An integrated intensity ratio of the superlattice to fundamental reflection gives eq. (7). Therefore, we can determine the values of β_{Al} and β_X in principle from a set of eq. (7), i.e. based on at least two integrated intensity ratios. The rest of four unknown parameters, α_{Ti} , α_{Al} , α_X and β_{Ti} , can be determined with the aid of eqs. (4) and (5).

In these analytical procedures, each atomic scattering factor for a measured reflection angle was evaluated by interpolating the tabulated values⁽¹³⁾.

The temperature factor was evaluated by the following equation⁽¹⁴⁾:

$$\begin{aligned} T(\theta) &= \exp(-2M) \\ M &= \frac{1.14 \times 10^4}{M_a \times \Theta} \times \frac{\sin^2 \theta}{\lambda^2} \times \left\{ \frac{1}{4} + \frac{T}{\Theta} \phi\left(\frac{\Theta}{T}\right) \right\} \\ \phi\left(\frac{\Theta}{T}\right) &= \frac{T}{\Theta} \int_0^{\Theta/T} \frac{y dy}{\exp(y) - 1}, \end{aligned} \quad (8)$$

where M_a is the atomic weight and Θ is the Debye temperature⁽¹⁵⁾. We took account of the chemical composition of the alloy in estimating M_a and Θ .

IV. Results and Discussion

1. Chemical composition

Table 1 summarizes the average chemical composition of TiAl-X (X=V, Mn, Zr and Nb) alloys. Statistical variations in the determination of the chemical composition by EDAX were much below 10% (0.3–0.4% for Ti, 0.3–0.5% for Al, 2.5–3.5% for V and Mn, 2.0–3.0% for Zr and Nb). Generally, the chemical analysis with statistical variations below 10% is acceptable. Probability errors of the chemical composition, i.e. deviations exceeding a probability of 1/2, were within ± 0.1 at% for Ti and Al, and ± 0.05 at% for the third elements. Hereafter, we refer to the sample with 3.5 at% V as 3.5 V.

2. X-ray diffractometry

Table 2 tabulates Bragg angles of the reflections (001), (110), (201), (222) and integrated intensity ratios of the superlattice to fundamental reflections, $I_s/I_{(222)}$. The integrated intensities for reflections other than (201) were twice as large as that for the reflection (201) (≈ 9000 cps). The probability errors in the integrated intensity ratios ranged from 3×10^{-4} to 1×10^{-3} for all samples. Experimental errors in the Bragg angles (smaller than 1×10^{-4} degree) are neglected for all reflections.

Table 1 Chemical composition of TiAl-X (X=V, Mn, Zr and Nb) alloys.

Alloy	Concentration (at%)		
	Ti	Al	X
Ti-47.8Al	50.40	49.60	
3.5V	47.99	48.49	3.52
5V	47.48	47.39	5.13
2.5Mn	49.19	48.50	2.31
5Mn	48.79	46.80	4.41
2.5Zr	47.20	50.10	2.70
5Zr	44.90	48.60	6.50
2.5Nb	49.31	48.50	2.19
5Nb	46.79	47.69	5.52

Table 2 Bragg angle of (h, k, l) reflections for each alloy and the intensity ratio of superlattice to fundamental reflection, $I_s/I_{(222)}$.

Alloy	(hkl)	Bragg angle	$H=I_s/I_{(222)}$
3.5V	(001)	10.898	0.7754 ± 0.0006
	(110)	15.834	0.6467 ± 0.0006
	(201)	25.456	0.2990 ± 0.0003
	(222)	41.642	
2.5Mn	(001)	10.936	0.7522 ± 0.0009
	(110)	15.790	0.6363 ± 0.0008
	(201)	25.410	0.2945 ± 0.0003
	(222)	41.580	
2.5Zr	(001)	10.874	0.8824 ± 0.0007
	(110)	15.688	0.7417 ± 0.0006
	(201)	25.250	0.3454 ± 0.0006
	(222)	41.300	
2.5Nb	(001)	10.870	0.9188 ± 0.0004
	(110)	15.730	0.7708 ± 0.0004
	(201)	25.320	0.3574 ± 0.0007
	(222)	41.434	

3. Analysis of occupation sites

The values of P and Q in eq. (7) are determined using the values of atomic scattering factor, chemical composition, Bragg angle and intensity ratio for each sample (Tables 1 and 2). Using these values, the relationship between β_{Al} and β_X in the $\beta(Al)$ site is obtained for the TiAl-3.5 V alloy (Fig. 3). The figure reveals that the three lines for the integrated intensity ratios do not cross at one point but at three points because of errors in P and Q . Nevertheless, we can see that the V atom principally occupies the Al site because the β_V values of the three points are larger than $(1/2)C_V$ in the TiAl-phase (see eq. 4). Considering that the center of the gravity of the triangle formed by connecting these three points should yield some reasonable values of β_V and β_{Al} , we obtain $\beta_V=2.59$ at% and $\beta_{Al}=45.57$ at%.

Table 3 tabulates the values of β_X and β_{Al} for all the samples; the table shows that the V and Mn atoms preferentially occupy the Al site irrespective of the concentration ($(1/2)C_X < \beta_X < C_X$), whereas the Zr and Nb

Fig. 3 Relationship between β_{Al} and β_V in the $\beta(Al)$ -site for TiAl-3.5V alloy. Three lines are given by eq. (6) using various intensity ratios I_s/I_f . line ①: $I_s/I_f=I_{(001)}/I_{(222)}$, line ②: $I_{(110)}/I_{(222)}$, line ③: $I_{(201)}/I_{(222)}$.Table 3 Total concentration of X(C_X) and atomic concentration of Al(β_{Al}) as well as X(β_X) in the $\beta(Al)$ -sites for TiAl-X (X=V, Mn, Zr and Nb) alloys.

Alloy	C_X (at%)	β_X (at%)	β_{Al} (at%)
Ti-47.8Al			45.70
3.5V	3.52	2.59	45.57
5V	5.13	4.30	45.34
2.5Mn	2.31	1.52	45.45
5Mn	4.41	2.91	43.87
2.5Zr	2.70	0.47	46.69
5Zr	6.50	0.37	44.25
2.5Nb	2.19	0.64	47.18
5Nb	5.52	0.85	44.60

atoms occupy almost the Ti site ($0 < \beta_X < 1/3C_X$).

4. Analysis of ordered structures

The concentrations of Ti, Al and X (=Zr, Nb, V, Mn) in the Ti and Al sites are evaluated based on eqs. (4) and (5), using the values of β_X and β_{Al} (Table 3). Figure 4 shows the occupation ratios of the constituent elements in both sites against the concentrations of the third elements; the x-axis and the y-axis represent the concentration of the third element and those of Ti, Al and X in both sites, respectively. White and black marks show the concentrations of the elements in the Ti and Al sites, and vertical lines on the marks show the magnitudes of experimental errors to be explained later; marks without vertical lines indicate smaller experimental errors. The

Fig. 4 Occupancy variation of each atom in both sites vs the concentration of third elements X in TiAl-phase. $\circ$ (Ti), $\square$ (Al) and $\triangle$ (X) for the α (Ti)-site, $\bullet$ (Ti), $\blacksquare$ (Al) and $\blacktriangle$ (X) for the β (Al)-site, $\odot$ and $\boxtimes$ indicate the concentration of Ti and Al.

diagrams in the second row show the concentrations of Ti in the Ti site and Al in the Al site (right site). The third diagrams show the concentrations of Ti in the Al site and Al in the Ti site (wrong site), and the fourth diagrams give the concentration of X in the Ti or Al site; the concentrations of Ti and Al are shown in the first row of Fig. 4.

Judging from the fourth diagrams of Fig. 4, we conjecture that most of the Zr and Nb atoms occupy preferentially the Ti site, whereas most of the V and Mn atoms occupy the Al site.

When we carefully examine the concentration changes of Ti or Al in the right or wrong site as the third elements

are dissolved, we notice that the concentration of Ti in the Ti site significantly decreases with increasing concentration of Zr in the TiAl-Zr alloy. This indicates that the Zr atoms substitute for the Ti atoms, pushing Ti atoms out of the Ti site into the Al site. Thus, the concentration of Ti in the right site decreases, and consequently the degree of order decreases in the TiAl-Zr alloy.

In the TiAl-Nb alloy, the Nb atoms substitute for both Ti and Al atoms in the wrong sites at a low concentration of Nb pushing them into the right sites, which results in an increase in the degree of order. However, at a higher concentration of Nb, only substitution for Ti in the right site takes place, which leads to a decrease in the degree of

order in contrast to the situation at a lower Nb concentration.

For the TiAl-V alloy, the concentration of Ti or Al in the wrong site decreases while the concentration of Ti in the right site increases with increasing concentration of V, resulting in increasing the degree of order.

The situation for the TiAl-2.5Mn alloy is the same as that for the TiAl-V alloy. For a concentration of Mn higher than 2.5at%, however, the mode of site occupation changes; Mn atoms substitute even for Ti and Al in the right sites leading to a decrease in the degree of order below that of the 2.5Mn alloy.

5. Experimental errors

The errors indicated by the vertical lines on the marks in Fig. 4, are composed of the errors in intensity and composition measurements, ΔH and ΔC_j . These errors have some effect on the P -value (no effect on the Q -value) in eq. (7), as shown by eqs. (6) and (6').

Assuming that ΔP is due to ΔH and ΔC_j , we obtain the following equation for ΔP , by differentiating eq. (6) with respect to H and C_j ,

$$\Delta P = \Delta P_H + \Delta P_C$$

$$= D \left\{ \frac{1}{2} \sqrt{\frac{H}{Y}} \sum f_j(\theta_i) C_j \right\} \frac{\Delta H}{H} + D \left\{ \sqrt{\frac{H}{Y}} \sum f_j(\theta_i) \Delta C_j - \sum f_j(\theta_s) \Delta C_j \right\},$$

where

$$D = \frac{1}{2 \{ f_{Ti}(\theta_s) - f_{Al}(\theta_s) \}}$$

and

$$Y = m \times T \times L.$$

ΔP_H and ΔP_C correspond to the errors in ΔP that are caused by ΔH and ΔC_j , respectively. For the TiAl-3.5V alloy (Fig. 3), it holds that $|\Delta P_H| \leq 0.01$ at% for any of the three lines in the figure, and $|\Delta P_C| \leq 0.04$ at%, from $\Delta C_{Ti} \leq 0.1$ at%, $\Delta C_{Al} \leq 0.1$ at% and $\Delta C_V \leq 0.05$ at% under the condition $\Sigma \Delta C_j = 0$. The effect of compositional errors on the temperature factor, $T(\theta)$, was neglected, because the error in the temperature factor, $\Delta T(\theta)$, caused by ΔC_j was much smaller than by ΔP_C .

When we take account of ΔP_H alone with $\Delta P_C = 0$, the lines ①, ② and ③ in Fig. 3 can be redrawn as the bands with a width of ΔP_H as shown in Fig. 5; the central black region corresponds to the area which is formed by all these three bands. This black region is moved upwards or downwards as a hatched area as ΔP_C is increased or decreased to ± 0.04 at%. In view of both errors in the intensity- and composition-measurements, we can consider that the existence region of (β_X, β_{Al}) is within the polygon (a-b-c-d-e-f-g-a) for the TiAl-3.5V alloy. The error regions for β_{Ti} , α_{Ti} , α_{Al} and α_X , can be evaluated with the aid of eqs. (4) and (5) as the coordinates $(\beta_{Al}$ and $\beta_X)$ go round this polygon.

When we look at the magnitudes of errors in Fig. 4(a)-(d), we find that (1) the error in the occupation ratio for V or Mn is larger than that for Zr or Nb, and (2) the corresponding error for Ti is much larger than that for Al in the alloy containing V or Mn, whereas this does not hold for the alloy containing Zr or Nb.

As for the item (1) we consider, for simplicity, a crossing point of the two lines; $\beta_{Al} = P_1 + Q_1 \times \beta_X$ and $\beta_{Al} = P_2 + Q_2 \times \beta_X$, where the subscript 1 or 2 represents the reflection line. The degree of shift of the crossing point is given by;

Fig. 5 Effect of errors in composition and intensity on β_{Al} and β_V in the β_{Al} -site for TiAl-3.5V alloy; errors are indicated by broadening of each line for composition (①'-①'', ②'-②'', ③'-③'') and intensity (①, ②, ③) measurements. The additional error in composition measurements expands the central black area which indicates the most probable values of β_{Al} and β_V in view of the error in intensity measurements alone, to the polygon (a-b-c-d-e-f-g-a).

Table 4 Values of Q which depend on superlattice reflections for TiAl-X (X=V and Zr) alloys, Q is defined by eq. (6') and ΔQ is the minimum among differences between Q 's.

Alloy	(h, k, l)	Q	ΔQ
3.5V	(001)	0.0235	0.0134
	(110)	0.0369	
	(201)	0.0591	
2.5Zr	(001)	1.9412	0.0441
	(110)	1.8290	
	(201)	1.8971	

$$|\Delta\beta_X| \leq \frac{|\Delta P_1| + |\Delta P_2|}{|Q_1 - Q_2|}$$

here, ΔP_1 or ΔP_2 , is the error in P_1 or P_2 . This shows that $\Delta\beta_X$ is inversely proportional to the difference between Q 's, which are roughly proportional to the difference in atomic number between Ti and X (eq. 6'). This situation manifests itself in the minimum value, ΔQ , for each alloy as shown in Table 4; in fact, the value of ΔQ for the Zr containing sample is larger than that for the V containing sample. Thus, the error, $\Delta\beta_X$ for the V or Mn containing sample is larger than that for the Zr or Nb containing sample.

As for the item (2), the error for Al or Ti is given by the error for X:

$$\begin{aligned} |\Delta\beta_{Al}| &= |Q \times \Delta\beta_X| \\ &= \left| \frac{f_{Ti}(\theta_s) - f_X(\theta_s)}{f_{Ti}(\theta_s) - f_{Al}(\theta_s)} \times \Delta\beta_X \right| \\ |\Delta\beta_{Ti}| &= \left| \frac{f_{Al}(\theta_s) - f_X(\theta_s)}{f_{Ti}(\theta_s) - f_{Al}(\theta_s)} \times \Delta\beta_X \right|. \end{aligned}$$

A comparison of $|\Delta\beta_{Ti}|$ with $|\Delta\beta_{Al}|$ leads to $|\Delta\beta_{Ti}| \gg |\Delta\beta_{Al}|$ for the V or Mn containing sample, whereas $|\Delta\beta_{Ti}| \approx |\Delta\beta_{Al}|$ for the Zr or Nb containing sample.

6. Application to other ternary alloys

We now consider the applicability of our method to other alloys with the $L1_0$ -type or any other structures. As mentioned above, the accuracy for determining the occupation sites and its ratios depends on ΔQ . First of all, in the light of Q -value, we should consider whether or not our method is appropriate to determine the occupation sites of the third element in various alloys.

As an alloy with the $L1_0$ -structure, we adopt the intermetallic compound CuAu I with the addition of Ni or Pd. When calculating the Q -value, we use atomic number, ZA , instead of an atomic scattering factor, f , because f is roughly proportional to ZA . We obtain $|Q| = |(28 - 29)/(79 - 29)| = 0.02$, and 0.34 for the addition of Ni and Pd, respectively. Thus, we can determine the occupation sites with a higher accuracy for Pd than Ni. We can also determine similarly the minimum Q -value among all the TiAl-X alloys in this study as 0.11 for the V addition.

As an example of the alloy with a different structure, let's take the intermetallic compound Ni_3Al ($L1_2$ -structure) with some third elements. The structure factor for Ni_3Al is $|3f_\alpha + f_\beta|$ and $|f_\beta - f_\alpha|$ for the fundamental and superlattice reflections, respectively. Setting $\Sigma\alpha_j = 0.75$ and $\Sigma\beta_j = 0.25$ in eq. (5) leads to an equation corresponding to eq. (7). In this case, the equation for the Q -value is as follows:

$$Q = \frac{Z(f_{fNi} - f_{fX}) + (f_{sNi} - f_{sX})}{Z(f_{fNi} - f_{fAl}) + (f_{sNi} - f_{sAl})} \quad \text{with} \quad Z = \left\{ \frac{H}{m \times T \times L} \right\}^{1/2}.$$

When the superlattice (201) and fundamental (222) reflections are measured for the addition of Mn, we obtain

$Z \approx 0.19$ and $Q \approx 0.25$. This confirms that our method is applicable to Ni_3Al with the $L1_2$ -structure.

7. Comparison with other studies

We compare our results with others obtained by X-ray diffractometry or ALCHEMI.

Karg *et al.* have determined by X-ray diffractometry the occupation ratio for Ni_3Al with 3 to 7 additional elements⁽³⁾. They measured an integrated intensity ratio and determined the occupation ratio of each element in such a way that the determined occupation ratio fits the measurement. However, there are a number of combinations for determining the occupation ratio in their fitting, so it is difficult to determine the occupation ratio of each element exactly.

Ferjani *et al.* have provided two parameters that are necessary to express the degree of long range order in Ni_3Fe -X ternary alloys, and these parameters are determined from the integrated intensity ratios, $I_{(100)}/I_{(200)}$, with CoK_α or CuK_α radiation⁽⁴⁾. Their method can determine in principle the occupation ratio of the constituent elements, by taking advantage of AXS for Ni_3Fe where there is a large or small difference in the atomic scattering factor between Ni and Fe, depending on CoK_α or CuK_α radiation.

Our proposed method is the same as that of Ferjani *et al.*, with regard to the determination of two unknown parameters that are necessary to express the occupation ratio in ternary alloys according to the integrated intensity ratios. However, our method does not make use of AXS. Instead, integrated intensity ratios are triply measured with a single CuK_α radiation, and are analyzed utilizing the angle dependence of the atomic scattering factor. For TiAl alloys, there are no available characteristic X-rays that can take advantage of AXS for Ti or Al; the addition of some kinds of third elements makes it possible to take advantage of AXS to some extent, but more experiments are required to improve the accuracy of site determination.

Konitzer *et al.*⁽⁵⁾ and Shindo *et al.*⁽⁶⁾ have determined the occupation sites of Nb in TiAl-Nb ternary alloys by ALCHEMI. Both results showed that Nb atoms occupy predominantly the Ti site, in agreement with our results. However, Konitzer *et al.* only determined the occupation sites of Nb atoms, with some quantitative results for the occupation ratio in both sites. On the other hand, Shindo *et al.* quantitatively determined the occupation ratio of each atom in both sites for the Al-43Ti-2Nb alloy, assuming non occupation ratio of Ti atoms in the Al site.

Morimura *et al.* have proposed a method for determining the occupation ratio in ordered alloys⁽⁷⁾, which is a combination of structure factor measurements and ALCHEMI; this method was applied without any assumptions to CuAu-Pd ternary alloys, in order to determine the occupation ratio in both sites.

The method of ALCHEMI needs some highly-advanced experimental techniques to prepare samples for electron microscopic observation as well as to determine the crystal direction exactly. In contrast to these disadvan-

tages, our proposed method is more advantageous because sample preparation is much easier and some average information about the whole sample is obtained without highly-advanced techniques. It is a future subject to apply both methods to an identical sample and check their availabilities.

V. Conclusions

With our proposed method, we could determine the occupation ratios of the third elements X (X=V, Mn, Zr, Nb), Ti and Al atoms in the Ti and Al sites for TiAl-X ternary alloys. The principal results are summarized as follows.

(1) Zr or Nb atoms occupy the Ti site, whereas V or Mn atoms occupy principally the Al site.

(2) In TiAl alloys with 5 at% Nb (Mn) and more than 2.5 at% Zr, the third elements substitute for Ti or Al atoms in the right sites, causing a decrease in the degree of order in the TiAl-phase.

(3) In alloys with 2.5 at% Nb (Mn) and more than 3.5 at% V, the third elements substitute for Ti or Al atoms in the wrong sites, and as a result of the Ti or Al atom being pushed into the right sites, the degree of order is increased.

(4) Errors in determination of the occupation ratio of the third elements depend on the difference in atomic number between Ti (or Al) and the third elements.

(5) Our method is advantageous in that the sample preparation is easy and an average information about the sample is obtained without any highly-advanced techniques. Furthermore, it is emphasized that our method is applicable to ternary alloys with crystal structures different from the L1₀-structure.

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