Site Determination of Fe, Co and Cr Atoms Added in Ni₃Al by Electron Channelling Enhanced Microanalysis*

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Atom location by channelling enhanced microanalysis (ALCHEMI) under a planar channelling condition was performed to locate the ternary additions Fe, Co and Cr of about 5 at% in the intermetallic compound Ni₃Al. It is concluded that the occupation site of Fe atoms depends on the chemical composition of the compound, i.e. the averaged Ni site occupancies of Fe in Ni₇₀Al₂₅Fe₅, Ni₇₂.₅Al₂₂.₅Fe₅ and Ni₇₅Al₂₀Fe₅ are 70%, 42% and 23%, respectively. The Ni site occupancy of Co in Ni₇₅Al₂₀Co₅ is 94%, but that of Cr in Ni₇₅Al₂₀Cr₅ is 6%, showing that Co and Cr have strong preferences in the Ni and Al sites, respectively. These results are compared with previous results obtained by APFIM and ALCHEMI under an axial channelling condition and the predictions from the thermodynamical consideration on the phase diagram. The accuracy of ALCHEMI under a planar channelling condition is also discussed for the L₁₂-type ordered structure.

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1. Introduction

The nickel aluminide such as Ni₃Al has been considered to be a promising high temperature structural material due to its superior mechanical properties. Despite of the superior strength, this material shows some brittleness. Aoki and Izumi(1) reported that the brittleness at room temperature was improved by the addition of boron. Recently the brittleness was also improved by the addition of some transition metals such as Fe and Mn(2)(3). In order to understand the mechanism of the improvement in the mechanical properties by substitutional additions, it is necessary to know the crystallographic occupation site of the additions in the compound structure. Ochiai et al.(4) investigated systematically the substitutional behavior of the transition metals in Ni₃Al and predicted the site preference from the extent of solubility lobes on the ternary phase diagrams. Recently the site occupation of the ternary additions Hf, Fe and Co has been investigated by atom probe field ion microscopy (APFIM)(5), and the atom location by electron channelling enhanced microanalysis (ALCHEMI) has been applied to the ternary compound under axial channelling conditions(6). The occupancy of Hf on the Al site has been determined to be 84.4% for Ni₇₆Al₂₃Hf₁ by APFIM and 87% for Ni₇₆Al₂₃Hf₃ by ALCHEMI under the <100> axial channelling condition, showing good agreement with each other. However, there are some differences between the two experiments; the occupancy of Co on the Al site was 0.5% by APFIM but 16% by ALCHEMI for Ni₇₀Al₂₅Co₅, and that of Fe was 42.6% by APFIM but 51% by ALCHEMI in Ni₇₅Al₂₁Fe₆. These results show that Hf and Co have a strong preference for the Al and Ni sites, respectively, while Fe has a weak preference for the Al sites.

In this paper it is intended to locate the additions of Fe, Co and Cr in Ni₃Al by means of ALCHEMI under a planar channelling condition, which has been previously applied in locating a ternary addition Nb in TiAl with the L₁₂-type ordered structure(7). Much attention was focused on the location of Fe atoms which has been reported to be both of the Ni and Al...
lattice sites with a slight preference for the latter as mentioned above. In order to make clear the dependence of the site occupancy of Fe on the composition of the host elements, we examined three specimens Ni$_{70}$Al$_{25}$Fe$_5$, Ni$_{72.5}$Al$_{22.5}$Fe$_5$, and Ni$_{75}$Al$_{20}$Fe$_5$. In addition, two other specimens containing 5 at% of Co and Cr were investigated in order to compare with the occupancy of Fe. For quantitative analysis, the formulation of the original ALCHEMI was modified for the L$_12$-type structure of Ni$_3$Al. The accuracy of ALCHEMI under a planar channelling condition was briefly discussed in comparison with that under axial channelling conditions.

II. Experimental

With pure nickel (99.9 mass%), aluminum (99.99 mass%) and the additions X (Fe(99.9 mass%), Cr(99.99 mass%), Co(99.9 mass%)), intermetallic compounds Ni-Al-X were prepared by melting in an arc furnace under argon atmosphere. The nominal contents of specimens are listed in Table 1. The bulk materials were annealed at 1273 K (1000°C) for 5 days and quenched into iced water. After slicing and polishing mechanically, the samples were electropolished with a solution of H$_2$SO$_4$: C$_2$H$_5$OH = 1:9.

We made the ALCHEMI study with a JEM 2000FX electron microscope equipped with the EDX (Energy Dispersive X-ray spectrometer) system. Selecting the areas so as to avoid crossing grain boundaries, the electron beam was focused to about 2 µm in diameter with the accelerating voltage 200 kV.

Since the Kikuchi lines were not so sharp due to the existence of lattice strain that we could not obtain the deviation parameter accurately. In order to find optimum diffraction conditions, we measured the X-ray spectra several times changing the excitation error around a superlattice reflection. Under the diffraction condition of $s > 0$ where $s$ is the deviation parameter, fundamental reflections tend to be incidentally excited strongly and the wave field corresponding to the spacing of superlattice reflections becomes weak. Hence, the superlattice reflection 110 was used instead of the 001 reflection, of which the neighboring fundamental reflections appear at a closer distance$^7$.

III. Formulation of ALCHEMI for the L$_12$-type Structure

The atomic arrangement of Ni$_3$Al having the L$_12$-type structure is shown in Fig. 1, where Ni and Al atoms are indicated by full and open circles, respectively. Here a projected atomic arrangement along the [001] direction is also shown. The incident electron beam is set nearly parallel to the (110) plane planes where two planes $\alpha$ and $\beta$ exist alternately, i.e. the plane $\alpha$ is composed of only Ni atoms while the $\beta$-plane is a mixed plane composed of both Ni and Al atoms.

For the L$_12$-type structure, the original ALCHEMI formulation$^8$ can be modified

![Fig. 1 Atomic arrangements of Ni$_3$Al with the L$_12$-type ordered structure, showing alternate (110) planes ($\alpha$ and $\beta$) parallel to the electron beam.](image-url)
under a planar condition as follows. As pointed out in the previous paper(7), we have to take account of the incidental occupation of host elements Ni(Al) into the antisite, i.e., Al(Ni) site due to the addition of the ternary elements, because the content of the additions, 5 at%, is not small enough to neglect its substitutional effect on the host elements. So X-ray intensities from the Ni, Al and additional element X, \( N_{Ni}^{(n)} \), \( N_{Al}^{(n)} \) and \( N_X^{(n)} \) for the diffraction conditions \( n=1 \), 2 and 3 can be given by

\[
N_{Ni}^{(n)} = P_{Ni} \cdot \{ A_{\alpha} \cdot I_{\alpha}^{(n)} + A_{\beta} \cdot I_{\beta}^{(n)} \} \\
N_{Al}^{(n)} = P_{Al} \cdot \{ B_{\alpha} \cdot I_{\alpha}^{(n)} + B_{\beta} \cdot I_{\beta}^{(n)} \} \\
N_X^{(n)} = P_X \cdot \{ C_{\alpha} \cdot I_{\alpha}^{(n)} + C_{\beta} \cdot I_{\beta}^{(n)} \} 
\]

\[
= P_X \cdot \left\{ \frac{2}{3} \cdot z \cdot k \cdot I_{\alpha}^{(n)} + \left( \frac{1}{3} \cdot z \cdot k + z \cdot (1-k) \right) \cdot I_{\beta}^{(n)} \right\}, (3)
\]

where \( I_{\alpha}^{(n)} \) and \( I_{\beta}^{(n)} \) are the thickness averaged density of incident electrons at the \( \alpha \)- and \( \beta \)-planes, respectively. The superscript \( (n) \) indicates the three diffraction conditions, i.e. \( n=1 \) for \( s>0 \), \( n=2 \) for \( s<0 \) and \( n=3 \) for a non-channelling condition. \( P_{Ni} \), \( P_{Al} \) and \( P_X \) are the scaling factors for taking account of the absorption and the difference of X-ray fluorescence yields of each element. \( A_{\alpha,\beta} \), \( B_{\alpha,\beta} \) and \( C_{\alpha,\beta} \) indicate the atomic ratios of Ni, Al and X in the \( \alpha \) and \( \beta \) planes, respectively. \( A_{\alpha,\beta} \) and \( B_{\alpha,\beta} \) are given for the three compounds I, II and III in Table 2, where \( x \), \( y \) and \( z \) indicate the atomic ratios of the constituents Ni, Al and X \((x+y+z=100)\). Here we take into account the antisite occupancy of the host elements, i.e. Al atoms in the Ni site in the compound I, and Ni atoms in the Al site in the compound III. As for the compound II, one of the coefficients \( A_{\alpha,\beta} \) and \( B_{\alpha,\beta} \) assigned to the compounds I and III is used depending on the substitutional behavior of the addition, i.e. if Fe favors the Al site, the coefficients for the compound I should be used, and otherwise those for the compound III should be used.

Eliminating the unknown parameters of \( P_{Ni,Al,X} \) and \( I_{\alpha,\beta}^{(n)} \) from the eqs. (1), (2) and (3), the atomic fraction of X at the Ni site is given by

\[
k = \frac{S-N_X}{\frac{2}{3} \cdot [ N_X \cdot (R^{(2)}-1) - S \cdot (R^{(1)}-1) ]}, (4)
\]

where

\[
N_X = \frac{N_{Ni}^{(1)}}{N_X^{(2)}},
\]

\[
R^{(n)} = \frac{A_{\beta} \cdot P - B_{\beta} \cdot N_{Ni}^{(n)}}{B_{\alpha} \cdot N_{Al}^{(n)} - A_{\alpha} \cdot P},
\]

\[
S = \frac{N_{Al}^{(1)} \cdot B_{\beta} + B_{\alpha} \cdot R^{(2)}}{N_{Al}^{(2)} \cdot B_{\beta} + B_{\alpha} \cdot R^{(1)}},
\]

and

\[
P = \frac{P_{Ni}}{P_{Al}} = \frac{N_{Ni}^{(3)}}{N_{Al}^{(3)}} \cdot \frac{B_{\alpha} + B_{\beta}}{A_{\alpha} + A_{\beta}}.
\]

As discussed in the previous paper(7), \( A_{\alpha,\beta} \) and \( B_{\alpha,\beta} \) depend on the unknown parameter \( k \) (Table 2), and \( R \) and \( S \) containing \( A_{\alpha,\beta} \) and \( B_{\alpha,\beta} \) are also unknown. Assigning an appropriate (dummy) number to \( k \) first, we estimated \( R \) and \( S \), and then obtained \( k \) from (4). This value was reinserted in (6), (7) and (8) to estimate \( R \) and \( S \) more accurately. These procedures were iterated a few times to obtain

| Specimens | Atomic ratio |
|-----------|--------------|
|           |   \( A_{\alpha} \) |   \( A_{\beta} \) |   \( B_{\alpha} \) |   \( B_{\beta} \) |
| I(II)     |  \( \frac{2}{3} \cdot x \) |  \( \frac{1}{3} \cdot x \) |  \( \frac{2}{3} \cdot (75-x-z \cdot k) \) | \( \frac{1}{3} (75-x-z \cdot k + (25-z \cdot (1-k)) \) |
| III(II)   |  \( \frac{2}{3} \cdot (75-z \cdot k) \) |  \( \frac{1}{3} \cdot (75-z \cdot k) + x-75+z \cdot k \) | 0 | \( y \) |
Experimental errors due to the counting statistics, $\Delta k$, are estimated to be
\[
\Delta k = \sum \left[ \frac{\partial k}{\partial N_{Ni}^{(n)}} \Delta N_{Ni}^{(n)} + \frac{\partial k}{\partial N_{Al}^{(n)}} \Delta N_{Al}^{(n)} + \frac{\partial k}{\partial N_{X}^{(n)}} \Delta N_{X}^{(n)} \right].
\]  
(9)

In the above equation, the sum is taken for the three different diffraction conditions $n=1$, 2 and 3, and $\Delta N$ is given by
\[
\Delta N = 3 \sqrt{N},
\]  
(10)

which shows the 99% confidence level.

### IV. Results

X-ray spectra were obtained around the systematic diffraction conditions, where a superlattice reflection 110 was strongly excited. The EDX spectra on the two diffraction conditions ($s>0$, $s<0$) are shown in Fig. 2, where the peak intensity of Al is set equal. Comparing the two, the X-ray intensity of Ni on the second diffraction condition ($s<0$) is much higher than that of the first one ($s>0$). The X-ray intensity of Fe also changes in the same way as that of Ni from one to the other. The difference directly shows the electron channeling effect under a planar channeling condition. In addition to these X-ray spectra, we also used X-ray intensities under a non-channeling condition ($n=3$) where no low order reflections were strongly excited.

With these X-ray spectra, we evaluated the site occupancy, $k$, of the ternary additions at the Ni site from (4). The results with statistical errors estimated from (9) are summarized in Table 1. It is shown that 94(±17)% Co atoms in Ni$_{70}$Al$_{25}$Co$_5$ occupy the Ni site, while 6(±17)% Cr atoms in Ni$_{75}$Al$_{20}$Cr$_5$ occupy the Ni site. This strong Ni site preference of Co atoms is consistent with the results by the AP-FIM(S) and the axial channeling experiments (6).

In contrast with the occupation of Co and Cr, Fe atoms tend to take both Ni and Al sites. In order to determine accurately the site occupancy of Fe, we measured several times the X-ray spectra from different crystal grains in the compounds containing Fe. Two typical evaluations are listed in Table 1. The averaged occupancies of Fe in the Ni site are 70(±12)%, 42(±15)% and 23(±15)% for the three compounds I, II and III, respectively, which decrease with decreasing Al concentration.

### V. Discussion

In this work, it has been shown that the site occupancy of Fe is strongly affected by the chemical composition of host elements. As for X=Co and Cr, we were unable to prepare three compounds of the L1$_2$-type structure with the compositions Ni$_{70}$Al$_{25}$X$_5$, Ni$_{75}$Al$_{20}$X$_5$ and Ni$_{75}$Al$_{20}$X$_5$ because of their small solubility limits. Consequently, we could not compare the composition dependence of
the site occupancy of these elements with Fe. Nevertheless, it may be concluded that Co has a stronger preference in the Ni site than Fe in Ni_{70}Al_{25}X_{5}, while Cr has a stronger preference in the Al site than Fe in Ni_{75}Al_{20}X_{5}.

Ochiai et al.\textsuperscript{(4)} investigated the substitution behavior of transition metals in the Ll2-type compounds Ni_{3}Al, Ni_{3}Ga and Ni_{3}Ge. Using the bonding energy $V(\text{Ni-Al})$, $V(\text{Ni-X})$ and $V(\text{Al-X})$ estimated from the Miedema’s semi-empirical formula\textsuperscript{(9)}\textsuperscript{(10)} for the heat of alloy formation, they obtained a function $U(X)$ for indicating the substitutional behavior of the element X in Ni_{3}Al,

$$U(X) = \frac{V(\text{Ni-X})}{V(\text{Ni-Al})} - \frac{V(\text{Al-X})}{V(\text{Ni-Al})}. \quad (11)$$

$U(X)<0$ indicates the preferential occupancy of an addition X on the Ni site while $U(X)>0$ shows preference on the Al site. According to their evaluations, $U(\text{Co})<0$, $U(\text{Fe})\leq 0$ and $U(\text{Cr})\geq 0$, and hence Co has a preference for the Ni site, and Cr and Fe have a preference for both sites. Although Cr has a preference for both Ni and Al sites, they obtained two relations $U(\text{Co})<U(\text{Fe})$ and $U(\text{Fe})<U(\text{Cr})$. These two relations agree well with our results obtained in the compounds Ni_{70}Al_{25}X_{5} and Ni_{75}Al_{20}X_{5}, respectively.

Finally we discuss the accuracy of ALCHEMI under a planar condition. In the previous paper\textsuperscript{(7)} on an intermetallic compound TiAl containing 2 at\% Nb, we discussed the accuracy of occupation probabilities determined by ALCHEMI which directly depends on the magnitude of the electron channelling effects. In the Ll0-type structure, there are alternate Ti and Al planes as shown in the Fig. 3, and hence the channelling effect occurs strongly in TiAl. We could locate 2 at\% of Nb within the statistical errors of several percents. Compared with TiAl, the channelling effect is not so strong in Ni_{3}Al due to the existence of the mixed plane (Fig. 1). As shown in Table 1, the statistical errors could hardly be made smaller than 10\% in this case. In order to overcome this, Bently\textsuperscript{(6)} used an axial channelling condition to locate the additions Hf, Fe and Co in Ni_{3}Al, and actually obtained the stronger electron channelling effects than our experiments. This is because there exist single Ni and Al atomic columns under the axial channelling condition with the incident beam parallel to the [100] or [111] direction. In these conditions, however, electron standing wave is so sharp due to the strongly excited many beam conditions that the delocalization effect is strongly enhanced\textsuperscript{(11)}, i.e. the excitement of electrons for the elements does not equally occur around nuclei and it is necessary to correct this effect for each element\textsuperscript{(6)}. Nevertheless, his experimental result was corrected by taking account of this delocalization effect consistently and agreed well with the present result, which was obtained without any correction for the delocalization effect.

**VI. Conclusion**

The above results are summarized as follows:

1. The ternary additions Fe, Co and Cr of 5 at\% in Ni_{3}Al are well located by ALCHEMI under a planar channelling condition with the statistical counting errors of about ±15\%.

2. From the quantitative analysis, it is shown that the occupation site of Fe depends strongly on the composition of the host elements. The averaged occupancies of Fe...
in the Ni site are 70%, 42% and 23% in the compounds Ni\textsubscript{70}Al\textsubscript{25}Fe\textsubscript{5}, Ni\textsubscript{72.5}Al\textsubscript{25}Fe\textsubscript{5} and Ni\textsubscript{75}Al\textsubscript{20}Fe\textsubscript{5}, respectively, with the statistical errors of ±12–15%.

(3) The Ni site occupancy of Co and Cr are 94% and 6% in the compound Ni\textsubscript{70}Al\textsubscript{25}Co\textsubscript{5} and Ni\textsubscript{75}Al\textsubscript{20}Cr\textsubscript{5}, respectively, with the statistical errors of ±17%.

(4) Weak preferences of Fe in both Ni and Al sites are in contrast to the strong preference of Co in the Ni site in Ni\textsubscript{70}Al\textsubscript{25}X\textsubscript{5} and that of Cr in the Al site in Ni\textsubscript{75}Al\textsubscript{20}X\textsubscript{5}, respectively.

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