THE ALLOYING BEHAVIOR OF BORON AND CARBON IN Ni_3Al [①]

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ABSTRACT   To further understand the alloying behavior for Ni_3Al, the alloying behavior of boron and carbon in Ni_3Al has been studied by X-ray powder diffraction analysis. The results show that boron and carbon occupy the octahedral interstitial site with six nearest neighboring nickel atoms in the $L1_2$-type structure, and the additives can increase the degree of long-range order for Ni_3Al, the degree of long-range order for Ni_3Al varies with the stoichiometry; the effects of boron and carbon on the lattice parameter of Ni_3Al are also evaluated. Comparatively, the degree of the long-range order is highest for Al-rich $Ni_{74}Al_{26}$ and it is lowest for Ni-rich $Ni_{76}Al_{24}$. The order degree for stoichiometric $Ni_{75}Al_{25}$ stands between them. Furthermore, the role of boron in increasing the degree of long-range order is more significant in Al-rich $Ni_{74}Al_{26}$ than in Ni-rich $Ni_{76}Al_{24}$ or stoichiometric $Ni_{75}Al_{25}$. With boron and carbon content increasing, the lattice parameter of Ni_3Al increases linearly, and the increment caused by carbon is more pronounced than that by boron. Moreover, the increasing trend of the lattice parameter by boron addition is followed by the stoichiometric sequence of $Ni_{76}Al_{24}$, $Ni_{75}Al_{25}$, $Ni_{74}Al_{26}$.

Key words intermetallics Ni_3Al stoichiometry   solid solution alloying   lattice parameter

1   INTRODUCTION

The solid solution alloy design relies on our understanding of the alloying behavior, i. e. the substituional or interstitial behavior of solute atoms and further the interaction between solutes with constituent atoms and defects in crystals. In case of Ni_3Al with microalloying addition, previous researches[1, 2] show that B and C atoms occupy the body-centered interstitial site of $L1_2$-type structure, while Be atoms occupy the Al site. And they all can enhance the further ordering of the constituent atoms. But unfortunately the mathematical approach used in above studies is incorrect somewhere. Considering it, in the present study the correct structural analyzing formulas for Ni_3Al were presented, and at the same time the alloying behavior of B and C as well as their effects on the lattice parameter in Ni_3Al were determined by the X-ray powder diffraction analysis. Besides, in order to obtain an extensive understanding of the alloying be-havior of B, the stoichiometric effect is system-atically analyzed. Finally, the mechanisms of the alloying behavior were discussed in terms of the crystal structure of Ni_3Al and the interaction be-tween the related atoms.

2   EXPERIMENTAL

The alloying elements added to Ni_3Al were boron (subgroup $3B$) and carbon (subgroup $4B$). Ni-rich Ni_3Al alloy was designed based on the following formula

$$(Ni_{76}Al_{24})_{100-x} B_x$$
or $$(Ni_{76}Al_{24})_{99.98-x} B_{0.02}C_x \tag{1}$$

The stoichiometric effect was considered by changing the ratio of Al/Ni for Ni_3Al. The re-sulted Ni_3Al alloy plates (170 mm × 70 mm × 15 mm) were prepared by induction melting and di-rectional solidification and then were homoge-nized at 1373 K in air for 2 d followed by furnace cooling. The discrepancies between the designed and analyzed chemical composition of the pre-

pared alloys were very small (relative error is $\pm$ 0. 3%). Therefore, the nominal composition was used in the following analysis.

The Ni_3Al powders for the X-ray diffraction analysis with particle diameter less than 74 μm were prepared by a filing process and then annealed at 1 173 K under a vacuum of 3×10^{-3} Pa for 1 d followed by furnace cooling. The intensities of the diffraction lines of (200) and (100) planes were measured by a Rigaku D/max-rA type X-ray diffratometer, and the related experimental conditions were: CuK_α radiation monochromatized with a graphite crystal, 40 kV accelerating voltage, 100 mA current density, stepped scan mode, $(1/2)°$ beam diverging slit, 0. 3 mm receiving slit, 0. 02° stepping angle and 10 s data sampling time. Finally, the lattice parameter of Ni_3Al alloys was obtained by the determination of the (311) peak position using CrK_{β_1} radiation.

3　PRINCIPLE AND STRUCTURE ANALYSIS

In ordered Ni_3Al alloy, the relative intensity of the fundamental reflections to those of the superlattice ones can be affected by such factors as the point defects induced by the constituent atoms, i. e. , vacancies, interstitials and anti-site defects, and the site occupation and concentration of alloying atoms. Therefore, by comparing the calculated relative intensities with the experimental ones, we can derive the information on the site occupation of alloying atoms and the related variation in the long-range-order degree for Ni_3Al alloys.

The integrated intensity ratio I_{200}/I_{100} of the fundamental to superlattice reflections is given for structure analysis as follows:

$$\frac{I_{200}}{I_{100}} = \frac{| F_{200} |^2 (LP)_{200} (e^{-2Mn})_{200}}{| F_{100} |^2 (LP)_{100} (e^{-2Mn})_{100}} \qquad (2)$$

where F is the structural factor, LP is the Lorentz polarization factor and e^{-2Mn} is the temperature factor for atom n.

As the formation energy of vacancies or interstitials is about 2 times higher than that of the anti-site defects in Ni_3Al[3], it is reasonably sup-

posed that most of the point defects induced by the off-stoichiometry or non-equilibrium take the form of anti-site defects. Here we introduce a parameter y to represent the fraction of Al atoms in a unit cell of Ni_3Al wrongly occupying the Ni site. And at the same time the effect of the induced point defects on the ordered structure of Ni_3Al can also be described by the long-range-order degree S. Therefore, the structural factor of $Ni_{76}Al_{24}$ can be expressed as follows:

$$F_{200} = (1/25)(24f_{Al} + 76f_{Ni}) \qquad (3)$$

$$F_{100} = (24/25 - (4/3)y) \cdot$$
$$(f_{Al} - f_{Ni}) \qquad (4)$$

or $\quad F_{100} = S(f_{Al} - f_{Ni}) \qquad (5)$

where f_{Al} and f_{Ni} are the atomic scattering factors of Al and Ni, respectively. It should be noted that the multiplier of the parameter y in eq. (4) is different from that in references[1, 2].

B and C atoms in Ni_3Al are most likely to occupy octahedral interstitial sites which provide the largest volume for occupation. Furthermore, two different octahedral sites can be differentiated by the surrounding chemical environment, i. e. site I with six nearest neighboring Ni atoms and site II with four nearest neighboring Ni atoms and two Al atoms. When B and C atoms occupy site I or site II, the structure factor of $Ni_{76}Al_{24}$-B-C alloy designed by formula (1) can be expressed as follows:

$$F_{200} = (1/25)(24f_{Al} + 76f_{Ni}) +$$
$$n_Bf_B + n_cf_C \quad \text{site I and II (6)}$$

$$F_{100} = (24/25 - (4/3)y)(f_{Al} - f_{Ni}) -$$
$$n_Bf_B - n_cf_C \quad \text{site I} \qquad (7)$$

$$F_{100} = (24/25 - (4/3)y)(f_{Al} - f_{Ni}) +$$
$$(n_B3)/f_B + (n_C/3)f_C \quad \text{site II (8)}$$

or $\quad F_{100} = S(f_{Al} - f_{Ni}) -$
$$n_Bf_B - n_cf_C \quad \text{site I} \qquad (9)$$

$$F_{100} = S(f_{Al} - f_{Ni}) +$$
$$(n_B/3)f_B + (n_C/3)f_C \quad \text{site II}$$
$$(10)$$

where n_B and n_C are the number of B and C atoms in a unit cell of Ni_3Al , respectively; f_B and f_C the atomic scattering factors of B and C, respectively.

In the present study, the ratios of I_{200}/I_{100}

under two different ordering conditions were cal-culated. The first was assumed that the long-range-order degree for Ni₃Al was a constant(i. e. y or S is a constant), independent of the alloy-ing addition; the second was that the long-range-order degree varied with the alloying elements and their concentration. Finally, to check the validity of the simulation values, a method for calculating the long-range-order degree for Ni₃Al in a perfect ordering state should be given as a function of the site occupation behavior of atoms. Provided that in Ni₃Al there exited two types of sublattice referred to as β(site Ni) and α(site Al), respectively, and parameters $P_{1\beta}^{\beta}$ and $P_{i\beta}^{\beta}$ represented the probabilities of the con-stituent i which was of sublattice β occupying sublattice β and α, respectively, the long-range order degree could be expressed as:

$$S = \sum_{i=1}^{n}(P_{1\beta}^{\beta} - P_{i\beta}^{\beta}) \tag{11}$$

4　RESULTS

4. 1　Alloying behavior

The effect of B addition on the ratio of I_{200}/I_{100} for Ni₇₄Al₂₆ is shown in Fig. 1. In Fig. 1(a), the values of S or y corresponding to data points are calculated by the observed ratios of I_{200}/I_{100} and eq. (6), (7) and (9) provided B atoms occupy site Ⅰ; in Fig. 1(b), the values of S or y corresponding to data points are calculated by the observed ratio of I_{200}/I_{100} and eq. (6), (8) and (10) provided B atoms occupy site Ⅱ. Two dashed lines in the figure represent the variations of the theoretical ratio of I_{200}/I_{100} with B concentration on condition that Ni₇₄Al₂₆ is perfectly ordered (y = 0(S = 0. 987)) and its long-range-order degree is kept constant (y = 0. 007 40(S = 0. 987)) , respectively. On one hand, it is evident from Fig. 1(b) that B atoms are not likely to occupy site Ⅱ as in contract with observed reduction in the ratio of I_{200}/I_{100}, the theoretical ratio increases with B concentra-tion, In addition, the simulation value S (0. 988) is larger than the theoretical value S (= 0. 987) for the perfectly ordered Ni₇₄Al₂₆ contain-ing B, at the same time, the corresponding

number of Al anti-site defects y (= − 0. 001 14) is a negative. Such values of S and y are unreal-istic, On the other hand, it is shown from Fig. 1 (a) that if B atoms occupy site Ⅰ the theoretical ratio of I_{200}/I_{100} decreases with B concentration, which agrees well with the observed tendency of the ratio of I_{200}/I_{100}. Besides, B atoms occupy-ing site Ⅰ can further increase the long-range-order degree (or decrease y value) for Ni₇₄Al₂₆. According to the above analysis, in Ni₃Al B atoms are likely to occupy interstitial site Ⅰ rather than site Ⅱ. On the basis of the same ap-proach, we can see that when B atoms are added to Ni₇₅Al₂₅ and Ni₇₆Al₂₄ and C atoms to (Ni₇₆ Al₂₄)₁₀₀₋ₓBₓ, both B and C atoms occupy inter-stitial site Ⅰ, decrease the ratio of I_{200}/I_{100} for Ni₃Al and enhance further ordering of the con-stituent atoms of Ni and Al, shown in Fig. 2 and 3, respectively.

4. 2　Lattice parameter

The effect of B and C addition on the lattice parameter of Ni₃Al is shown in Fig. 4. The lat-
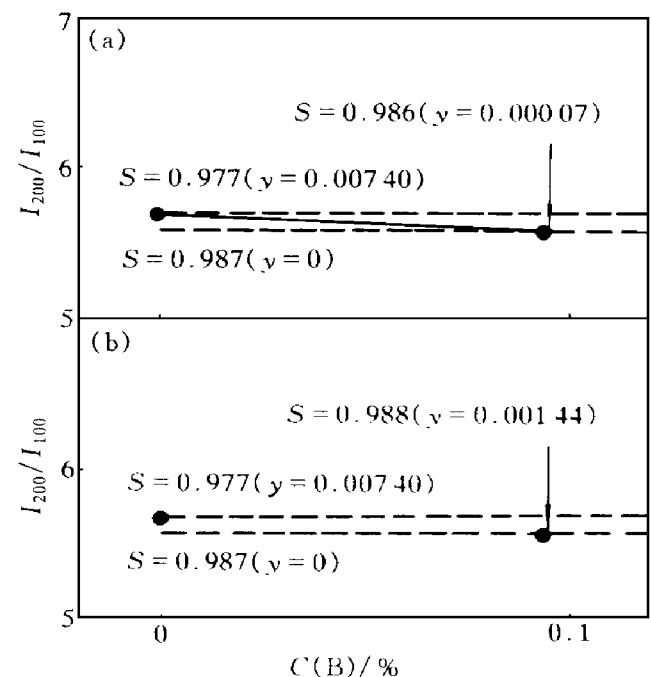

Fig. 1　Comparison between observed and calculated intensity ratios I_{200}/I_{100} of Ni₇₄Al₂₆ with addition of B in different sites
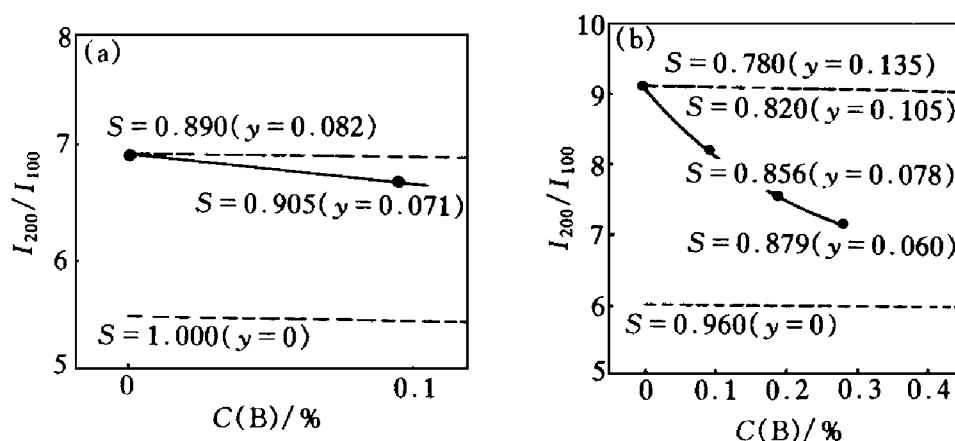
1 —site Ⅰ ; 2 —site Ⅱ

Fig. 2　Influence of addition of B on observed intensity ratio I_{200}/I_{100}

(a) —$(Ni_{75}Al_2)_{100-x}B_x$; (b) —$(Ni_{76}Al_{24})_{100-x}B_x$

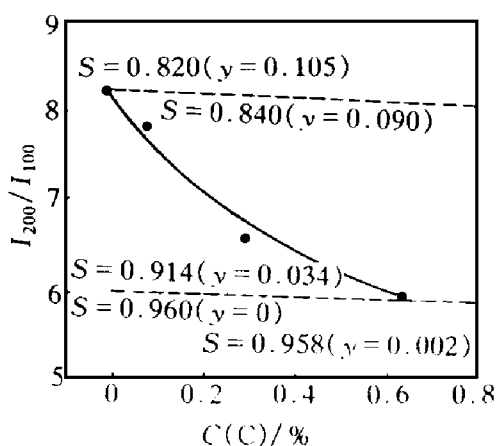**Fig. 3　Influence of addition of C on observed intensity ratio I_{200}/I_{100} of $(Ni_{76}Al_{24})_{100-x}B_x$(site I)**
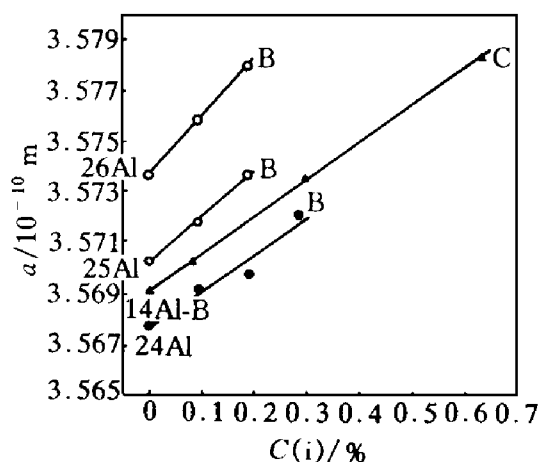

Fig. 4　Variation of lattice parameters of Ni_3Al alloys with addition of B or C atoms

tice parameter increases almost linearly with B or C content increasing, which also suggests that the amount of alloying addition is within its solid solution limit. Comparatively, the increment of lattice parameter of $Ni_{76}Al_{24}$ caused by C addition is more noticeable than that by B addition. Besides, the tendency of B addition to increase the lattice parameter is followed by the stoichiometric sequence of $Ni_{76}Al_{24} < Ni_{75}Al_{25} < Ni_{74}Al_{26}$.

5　DISCUSSION

It is recognized from the experiments that the observed order degree is largest for Al-rich $Ni_{74}Al_{26}$ ($S = 0.977$) and it is smallest for Ni-

rich $Ni_{76}Al_{24}$($S = 0.780$). The order degree for stoichiometric $Ni_{75}Al_{25}$($S = 0.890$) stands between them. In addition, all the observed order degrees are lower than those for the perfectly ordered $Ni_{74}Al_{26}$, $Ni_{75}Al_{25}$ and $Ni_{76}Al_{24}$($S = 0.987$, 1.000 and 0.960, respectively). This observation is consistent with the work done by Pope et al[4], which shows the long-range-order degree for stoichiometric Ni_3Al measured in a temperature range of 298~ 1 273 K is less than 1.000. Moreover, B and C addition can enhance the further ordering of the constituent atoms in Ni_3Al thereby stabilizing the $L1_2$ type structure. To evaluate the effect of alloying atoms on the long-range-order degree for Ni_3Al, the order degree ratio is defined as $K = (S_A - S)/(S_T - S)$, where S is the long-range-order degree for

Ni₃Al without alloying addition, S_A for Ni₃Al with alloying addition and S_T for the corresponding perfectly ordered Ni₃Al alloy (calculated by eq. (11)). Fig. 5 shows the effect of B and C addition on the order degree ratio(K) for Ni₃Al, where the stoichiometric effect is also included. It is found that the role of B in increasing the order degree is more noticeable in Al-rich Ni₇₄Al₂₆ than in stoichiometric Ni₇₅Al₂₅ or Ni-rich Ni₇₆Al₂₄. Besides, in the case of Ni₇₆Al₂₄ alloy, the role of C is equivalent to that of B. Furthermore, the effect of B and C on the long-range order degree for Ni₃Al is analyzed in terms of the site occupation of the additives and the interaction between the additives with the constituents (measured by the atomic bond energy E). According to Miedema's formula[5] for successfully calculating the formation energy of compounds, the bond energy between Ni and B or C atoms in Ni₃Al are calculated to be[2] $E_{NiB}= - 90. 5$ kJ/ mol and $E_{NiC}= - 104. 5$ kJ/ mol. These values are much less than those of bond energy between constituent atoms ($E_{NiAl}= - 74. 0$kJ/ mol, $E_{NiNi} = - 71. 3$ kJ/ mol and $E_{AlAl}= - 54. 5$ kJ/ mol), which suggests that there exits stronger attraction of Ni atoms for B or C atoms. Therefore, the B and C atoms at the octahedral interstitial site in the $L 1_2$-type structure tend to form strong bonding with their nearest neighboring Ni atoms and at the same time push Al atoms from wrongly occupying the nearest neighboring site back to the correct next nearest neighboring site, thereby stabilizing the $L 1_2$-type structure and enhancing the order degree. In addition, it is noted that the atomic bond energy varies with the ratio of constituent atoms for Ni₃Al . For example, when the ratio of Al/ Ni is raised to 1(i. e. NiAl), the bond energy is altered to be that $E_{NiB}= - 92. 9$ kJ/ mole and $E_{NiAl}= - 74. 7$ kJ/ mole. The tendency of the bond energy to increase with ratio of Al/ Ni increasing shows that there exits stronger mutual attraction between Ni and Al atoms as well as Ni and B atoms in Al-rich alloys than in Ni-rich ones. Hence, it can be

predicted that Al-rich alloys have a higher thermostability, i. e. a higher order degree. This prediction is in accordance with the experimental rules of the long-range order degree for Ni₃Al affected by the stoichiometry and B addition.
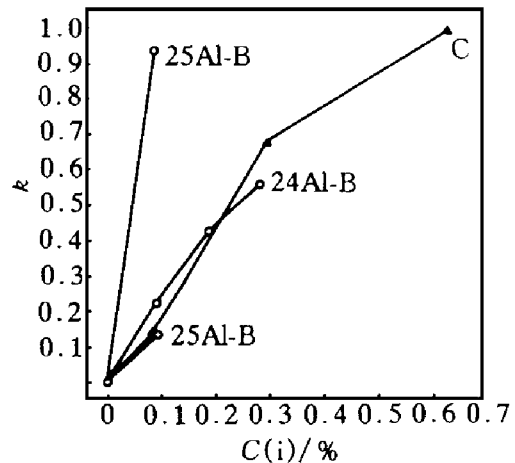

Fig. 5   Influences of B or C content and stoichiometry on long-range order degree ratio for Ni₃Al

6   CONCLUSIONS

(1) Alloying atoms B and C occupy the octahedral interstitial site with six nearest neighboring Ni atoms in Ni₃Al and they all can significantly enhance the long-range order degree for Ni₃Al.

(2) Comparatively, the long-range order degree is highest for Al-rich Ni₇₄Al₂₆ and it is lowest for Ni₇₆Al₂₄. The order degree for stoichiometric Ni₇₅Al₂₅ stands between them. Moreover, the role of B in increasing the long-range order degree is more noticeable in Al-rich Ni₇₄Al₂₆ than in Ni-rich Ni₇₆Al₂₄ or stoichiometric Ni₇₅Al₂₅.

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