Influence of Atomic Size Factors on the Phase Stability of Laves Phase in Nb-Cr-Ni-Al and Nb-V-Ni-Al Phase Diagrams

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Phase equilibria among the refractory bcc solid solution (bcc_{ss}), B2, and Laves phases in Nb-Cr-NiAl and Nb-V-NiAl isothermal sections were studied with the aim of introducing the NiAl-B2 phase and/or Al-containing Laves phase for improvement of the oxidation resistance of the bcc_{ss} phase as an Al reservoir layer for the Al_2O_3 surface layer. Laves phases appear in a wide composition range in both of the isothermal sections, which prevent equilibration of NiAl-B2 with the Nb-rich bcc_{ss} phase. The geometrical model proposed by Edwards was applied to understand the site-substitution behavior of the multi-component AB_2 Laves phase. In the Nb-Cr-NiAl, Nb-V-NiAl, and Nb-Mo-NiAl systems, the site-substitution behavior of the Laves phases could be explained by comparison of the average atomic diameters of NiAl-B2, Cr, V, and Mo. [doi:10.2320/matertrans.MJ201604]

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1. Introduction

Nb-based alloys are the most attractive refractory materials due to their high melting temperature and low density; however, they suffer from degradation by oxidation at high temperatures.^{1,2)} Niobium oxide scale is non-protective because the scale is composed of equilibrium phase, $\beta\text{-Nb}_2\text{O}_5$, which is porous and can easily cause cracking.³⁾ A number of studies have been conducted toward improvement of the oxidation resistance of Nb-based alloys. For example, Nb-based alloys composed of silicide phases such as Nb_5Si_3 and NbSi_2 or Laves phases have progressed in terms of oxidation resistance to some extent with SiO_2 -based coating; however, they have been reported to have insufficient oxidation resistance for practical application at operation temperatures above 1473 K.^{2,4)} B2 aluminide phases such as NiAl have also been investigated as coatings for Nb-based alloys.^{5,6)} They have been used as Al reservoir layers to maintain the Al_2O_3 surface layer in Ni-based superalloys. Similarly, some Laves phases containing Al are reported to enhance the oxidation resistance of NiAl-based alloys.⁷⁾ However, the formation of a brittle secondary reaction zone (SRZ) between Nb-based alloys and the NiAl layer has been observed, which may result in degradation of the components by spallation of the Al reservoir layer. This is due to the appearance of various ternary phases between NiAl-B2 and the Nb-bcc solid solution in the Nb-Ni-Al ternary phase diagram.^{8,9)}

The addition of elements to a bcc solid solution is one method to suppress formation of the SRZ. We have conducted a broad survey of X-Ni-Al (X: refractory elements) ternary systems, and several Ta-Ni-Al ternary phases are found between the Ta-bcc solid solution (bcc_{ss}) and NiAl-B2 phase, while a bcc_{ss} /NiAl-B2 two-phase field appears in the ternary X-Ni-Al (X = V, Cr, Mo, and W) systems.^{10–12)} C14 Laves phases with a wide composition range commonly appear in the Nb-Ni-Al and Ta-Ni-Al ternary phase diagrams,

and such a ternary Laves phase is a candidate for the brittle SRZ. Therefore, it can be expected that the addition of some elements such as V, Cr, Mo, or W to the Nb-Ni-Al system would suppress the formation of Laves phases. Among the quaternary systems composed of Ni and Al with refractory elements (V, Cr, Mo, and W) together with Nb or Ta, equilibrium of the bcc_{ss} /B2/Laves phase in quasi-ternary Ta-Cr-NiAl, Ta-V-NiAl, Ta-Mo-NiAl, and Nb-Mo-NiAl sections have been reported (Fig. 1).^{13–16)} It is suggested that $\text{Ta}(\text{Ni},\text{Al})_2\text{-C14}$ and TaCr_2 seem to be a continuous solid solution in the Ta-Cr-NiAl system (Fig. 1(a)), and in the sections of Ta-V-NiAl, the solubility of V in the $\text{Ta}(\text{Ni},\text{Al})_2$ Laves phase is quite large (Fig. 1(b)). These wide solubility ranges of Laves phases result in narrow bcc_{ss} /B2 two-phase fields that are limited to be almost along X-NiAl (X = V and Cr) lines. On the other hand, in the sections of Ta-Mo-NiAl

Fig. 1 bcc_{ss} /B2/Laves three-phase fields in quasi-ternary phase diagrams of the (a) Ta-Cr-NiAl,¹³⁾ (b) Ta-V-NiAl,¹⁴⁾ (c) Ta-Mo-NiAl,¹⁵⁾ and (d) Nb-Mo-NiAl¹⁶⁾ systems.

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and Nb-Mo-NiAl quasi-ternary systems (Figs. 1(c) and (d)), the limited substitution of Mo for Ta in $\text{Ta}(\text{Ni},\text{Al})_2$ -C14 and for Nb in $\text{Nb}(\text{Ni},\text{Al})_2$ -C14 results in wide $\text{bcc}_{\text{ss}}/\text{NiAl}$ -B2 two-phase fields. These quasi-ternary sections composed of Ni and Al with refractory elements commonly include a $\text{bcc}_{\text{ss}}/\text{B2}$ /Laves three-phase field, which suggests that the site-substitution behavior and solubility range of the Laves phase region governs the extent of the $\text{bcc}_{\text{ss}}/\text{NiAl}$ -B2 two-phase region. Schematics of the phase equilibria among the bcc_{ss} , B2, and Laves phases linked to the site-substitution behavior and solubility range of Laves phase are shown in Fig. 2. Figures 2(b) and (c) are sections of A-B-NiAl described in Fig. 2(a). Figure 2(b) shows the relationship between the continuous substitution of the B atom for Ni and Al atoms in the Laves phase, and the limited range of the $\text{bcc}_{\text{ss}}/\text{B2}$ two-phase field (Ta-V-NiAl and Ta-Cr-NiAl systems). On the other hand, Fig. 2(c) shows that limited substitution of the B atom for an A atom leads to a wide $\text{bcc}_{\text{ss}}/\text{B2}$ two-phase field (Ta-Mo-NiAl and Nb-Mo-NiAl systems).

However, the knowledge on the solubility and site-substitution behavior of elements in ternary and quaternary Laves phases is insufficient for discussion of the phase equilibria among the bcc_{ss} , NiAl-B2, and Laves phases in Nb-based alloys. Therefore, it is expected that investigations of phase equilibria related to Laves phases in higher order systems may provide valuable information not only for the development of alloys but also for fundamental alloy chemistry.

The stability of Laves phases has been explained in terms of atomic size factor and also valence electron concentration (VEC).^{17–19} In binary Laves phases, the most stable ratio of atomic diameters D_A/D_B is 1.225, determined by geometrical reasoning, and the range of the ratio is between 1.05 and 1.68.²⁰ The NbCr_2 Laves phase with a D_A/D_B ratio of 1.14 appears as a stable phase, although the D_A/D_B is rather smaller than the ideal value. On the other hand, NbV_2 has a

rather small D_A/D_B (1.09) compared to NbCr_2 ; therefore, NbV_2 does not appear as a stable phase.

The size factor is also expected to have a large effect on the site-substitution behavior of binary Laves phases. The arguments on the site-substitution behavior are related to the introduction of constitutional vacancies. However, some experimental methods, such as the ALCHEMI method, provide direct evidence for the site-substitution behavior of elements.^{21,22} The site occupancies of X (X = V, Mo, W, and Ti) in the NbCr_2 -C15 Laves phase of Nb-Cr-X systems were investigated using the ALCHEMI method, whereby V tends to substitute for Cr, while Mo, W, and Ti substitute for Nb.^{21,22} These results also confirm that the tendency of the solubility lobe is a good index to understand the site-substitution behavior in the NbCr_2 -C15 Laves phase. The atomic sizes of Mo, W, and Ti are close to Nb, while V is close to Cr; therefore, it can be concluded that the size factor is a key to understand the site-substitution behavior of Laves phases. According to previous studies,^{9,23} both Ni and Al tend to occupy the B-site of the AB_2 -type Laves phases $\text{Nb}(\text{Ni},\text{Al})_2$ and $\text{Ta}(\text{Ni},\text{Al})_2$. Figure 3 shows various Nb-based ternary systems with Cr, V, Ni, or Al. Each of these has C14 and/or C15 Laves phases. According to Nb-Cr-Al, Nb-Cr-Ni, and Nb-Al-Ni isothermal sections (Figs. 3(a)–(c)), wide compositional ranges of the $\text{Nb}(\text{Cr},\text{Al})_2$ and $\text{Nb}(\text{Cr},\text{Ni})_2$ ternary Laves phases have been identified,^{9,24,25} which suggests a wide Laves phase region in the Nb-Cr-Ni-Al quaternary system with a chemical description of $\text{Nb}(\text{Cr},\text{Ni},\text{Al})_2$. Such C14 Laves phases have been identified in Ni-Al-Cr-Mo-Nb alloys,^{26,27} and Zeumer and Sauthoff proposed to describe them as $\text{Nb}(\text{Cr}_{1-x-y}\text{Ni}_x\text{Al}_y)_2$.²⁸ Similarly, a $\text{Nb}(\text{Cr},\text{Ni})_2$ Laves phase with C14 structure was observed in the Ni-Al-Cr-Mo-Ti-Hf-Nb-W system.²⁹ Therefore, similar to the $\text{Ta}(\text{Ni},\text{Al})_2$ and TaCr_2 Laves phases in the Ta-Ni-Al-Cr quaternary system, a continuous solid solution between $\text{Nb}(\text{Ni},\text{Al})_2$ and NbCr_2 is expected. One purpose of the present study is thus to investigate the site-substitution behavior of Cr in the $\text{Nb}(\text{Ni},\text{Al})_2$ ternary Laves phase.

To understand the atomic size effect on the site-substitution behavior in the $\text{Nb}(\text{Ni},\text{Al})_2$ Laves phase, we have focused on V because its atomic size is slightly larger than Cr. Figure 3(d) shows the site-substitution behavior of V in NbCr_2 , and strongly suggests that V has a tendency to substitute for Cr in NbCr_2 because of its similar atomic size. Similar to NbCr_2 with Ni substitution, Ni-containing NbV_2 , i.e., $\text{Nb}(\text{V},\text{Ni})_2$, is reported to be a stable phase. Therefore, it is expected that similar to the expected extension of the Laves phase field with Cr addition to the Nb-Ni-Al system, V addition may result in the formation of $\text{Nb}(\text{V},\text{Ni},\text{Al})_2$ -C14 with a wide composition range in the Nb-V-Ni-Al system, although there is no information on the ternary Laves phases in the Nb-V-Al system. A comparison of the site-substitution behavior of V and Cr in the $\text{Nb}(\text{Ni},\text{Al})_2$ ternary Laves phase is thus a good example to understand and expand the atomic size effect on the stability of Laves phases.

Despite the above expectations, the site-substitution behavior of Laves phases composed of several elements including Al is not clearly understood, because the atomic diameter of Al evaluated from the pure Al structure is much larger than that of Cr, V, and Ni. The size of the Al atom in

Fig. 2 Schematics of phase equilibria among the bcc_{ss} , B2, and Laves phases. (a) A-B-Ni-Al quaternary phase diagram, (b) A-B-NiAl quasi-ternary section with a solubility lobe of Laves phase between $\text{A}(\text{Ni},\text{Al})_2$ and AB_2 , and (c) A-B-NiAl quasi-ternary section with a solubility lobe of Laves phase between $\text{A}(\text{Ni},\text{Al})_2$ and hypothetical 'B(Ni,Al)₂'.

Fig. 3 Isothermal sections of the (a) Nb-Cr-Al,²⁴⁾ (b) Nb-Cr-Ni,²⁵⁾ (c) Nb-Ni-Al,⁹⁾ and (d) Nb-Cr-V²¹⁾ systems.

some intermetallic compounds such as Ni_3Al and NiAl is smaller than that of pure Al.³⁰⁾ Therefore, in the present study, phase equilibria among bcc_{ss} , B2, and Laves phases in the Nb-Cr-NiAl and Nb-V-NiAl systems were investigated as good examples to understand not only the site-substitution behavior of Cr and V but also the site-substitution behavior of Al in Laves phase together with a transition metal element (Ni) by combining the direction and extent of solubility lobes in terms of the atomic diameter. The model proposed by Edwards is applied to understand the effect of the atomic size factor on the stability of Laves phase with Al.³¹⁾ Although Laves phases are commonly brittle at room temperature, Anton *et al.*³²⁾ concluded that materials based on the C14/C15 Laves phases, such as NbCr_2 and TaCr_2 , are potential candidates for high-temperature structural applications in the temperature range above 1273 K because of their high melting points. There have been various investigations on multiphase *in-situ* composites including Laves phases with the NiAl-B2 phase;³³⁾ however, the position of formation, size, and shape of Laves phases must be appropriately controlled to avoid brittle fracture of the materials. The results obtained through this study are expected to contribute to control of the Laves phase, and assist determination of whether to include or exclude them from materials composed of the bcc_{ss} and B2 aluminides.

2. Experimental Procedures

The nominal compositions of the alloys employed are listed in Table 1. To obtain Nb-X-NiAl (X = Cr and V) iso-

Table 1 Nominal compositions of the alloys employed (at%).

Alloy No.	Nb	Cr	V	Ni	Al
1	20	24		28	28
2	20	10		35	35
3	22.5		7.5	35	35
4	7.5		22.5	35	35

thermal sections, the nominal Ni composition was kept the same as the nominal Al composition. Alloys were prepared from high-purity raw materials (99.99% Ni, 99.99% Al, 99.99% Cr, 99.5% V, 99.9% Nb) by arc-melting repeated at least ten times with a non-consumable W electrode on a water-cooled copper hearth in an Ar atmosphere to ensure chemical homogeneity. Alloy ingots of ca. 20 g were cut using a wheel cutter, and some of the ingots were sealed in evacuated silica tubes for heat-treatment at 1473 K for 168 h, followed by water quenching. X-ray diffraction (XRD) analysis was conducted to identify the phases in the alloys. Microstructural observations and wave-length dispersive spectroscopy (WDS) for compositional analysis of the equilibrium phases in each sample were performed using field emission-scanning electron microscopy (FE-SEM; JEOL, JXA-8530F) equipped with electron probe micro-analysis (EPMA). It is generally difficult to determine the composition of phases with grain sizes less than the spatial resolution of the WDS instrumentation, which is typically ca. 1 μm . Therefore, to overcome this problem, WDS multi-point analyses were conducted. In this method, the typical

number of points for WDS point analysis was 100 points. These data obtained from three-phase alloys are either on the tie-line or within the tie-triangle in the ternary phase diagram. Therefore, multi-point analysis on multi-phase alloys is a powerful method to obtain α - β - γ tie-triangles for $\alpha/\beta/\gamma$ three-phase equilibrium of alloys with fine microstructure, and the data set allows the composition of the equilibrium phase to be deduced by application of the phase rule. This method was applied to some of the alloys with fine microstructure.³⁴⁾

3. Results

Figure 4 shows typical microstructures of Nb-Cr-Ni-Al and Nb-V-Ni-Al alloys, and the results of WDS multi-point analysis performed on the alloys are shown in Fig. 5 as isothermal sections of the quasi-ternary phase diagrams of Nb-Cr-NiAl and Nb-V-NiAl at 1473 K. In the Nb-Cr-Ni-Al alloys shown in Figs. 4(a) and (b), the Cr-bcc_{ss} phase (gray area), NiAl-B2 phase (dark area), and Nb(Cr,Ni,Al)₂-C14

phase (bright area) were confirmed by combining compositional analysis and XRD analysis results. An unknown phase (white area) was also identified. In the Nb-V-Ni-Al alloys shown in Figs. 4(c) and (d), the V-bcc_{ss} phase (gray area), NiAl-B2 phase (dark area), C14 phase (bright area), and unknown phases (white area) were confirmed. In the Nb-Ni-Al phase diagram, the Nb₇Ni₆ phase is reported to exhibit large Al solubility, with as high as 30.3 at% substitution for Ni (Fig. 3(c)).⁹⁾ The composition range of the Nb₇Ni₆ phase extends to 50 at% Nb in the Nb-Ni binary system, and the composition in the Nb-Ni-Al ternary system (46Nb-24Ni-30Al) also extends to Nb compositions lower than stoichiometry and which are close to the unknown phase (45Nb-3V-20Ni-32Al in at%) in alloy #3. Therefore, the unknown phase is probably Nb₇Ni₆ (W₆Fe₇-type structure) phase based on consideration of the composition of the unknown phase.

In Fig. 5, closed symbols denote the nominal compositions of alloys and open symbols denote results from WDS multi-point analysis. WDS multi-point analyses performed on the alloys provided information on the tie-lines between two-phase or three-phase equilibria within the tie-triangle. In Fig. 5(a), a single phase region of Laves phase lies along the line connecting Nb(Ni,Al)₂ and NbCr₂ in the Nb-Cr-NiAl system, which results in the Nb(Cr, Ni, Al)₂ quaternary Laves phase. The Nb composition of the Nb-lean side of the C14 phase is almost constant at ca. 30 at%. This value is consistent with the off-stoichiometric (Nb-lean) composition of binary NbCr₂-C15 (31.5 at% Nb), which has anti-site substitution of Cr.^{35,36)} The NiAl/bcc two-phase equilibrium was determined to appear only around the NiAl/Cr edge with quite a small amount of Nb in the bcc phase.

In Fig. 5(b), the single phase region of Laves phase in the Nb-V-NiAl system also seems to extend along a line connecting Nb(Ni,Al)₂ and hypothetical "NbV₂", which results in the Nb(V,Ni,Al)₂ quaternary Laves phase. However, the compositional region of the Laves phase deviates slightly toward the V corner. This tendency is similar with that for Ta(Ni,Al)₂-C14 in the Ta-V-NiAl system. The NiAl/bcc two-phase equilibrium also appears only around the NiAl/V edge with a small amount of Nb in the bcc phase.

Fig. 4 Microstructures of alloys after heat-treatment at 1473 K for 168 hours. (a) #1 Nb-24Cr-28Ni-28Al, (b) #2 Nb-10Cr-35Ni-35Al, (c) #3 Nb-7.5V-35Ni-35Al, and (d) #4 Nb-22.5V-35Ni-35Al.

Fig. 5 Compositional analysis results for (a) Nb-Cr-NiAl alloys after heat-treatment at 1473 K, and (b) Nb-V-NiAl alloys after heat-treatment at 1473 K. Alloy compositions are represented by closed symbols. The composition of the unknown phase in the Nb-V-Ni-Al alloy is not on the section of Nb-V-NiAl.

4. Discussion

The NiAl/bcc two-phase equilibrium appears only around the NiAl/Cr edge in the Nb-Cr-NiAl system and also around the NiAl/V edge in the Nb-V-NiAl system. The NiAl/bcc phase equilibria in these quaternary systems are limited by the extended solubility lobe of the Nb(NiAl)₂-C14 Laves phase with Cr and V substitution. The direction of the solubility lobes of the C14 phase in the Nb-Cr-NiAl and Nb-V-NiAl systems indicates that the preferential site of Ni, Cr, V, and Al is the B-site of the AB₂ Laves phase in these quaternary systems. This is consistent with the Ni and Al occupation of B-sites in the C14 phase³⁷⁾ of the Nb-Ni-Al ternary system and the preferential occupation of B-sites in the Laves phase by V and Cr in the Nb-Cr-V ternary system.^{21,22)}

To reveal the contribution of the atomic diameter ratio to the stability in the multi-component Laves phases, the average atomic diameters of A and B atoms must be estimated. The atomic sizes proposed by Goldschmidt have been traditionally used to examine the effect of atomic size on various aspects, such as Vegard's law for lattice constants and the stability of phases. Table 2 shows Goldschmidt diameters (coordination number (C.N.) = 12) for each element $D_{C.N.12}$, which are equal to twice the Goldschmidt radii ($D_{C.N.12} = 2R_{C.N.12}$) based on the size evaluated from the crystal structure and lattice constant(s) of the pure elements, together with the occupancy site in the NbCr₂ Laves phase. The order of $D_{C.N.12}$ seems to be strongly related to the occupancy; however, Al occupies Cr sites. The Goldschmidt diameter of

Al is estimated to be close to that for Nb and larger than that for Mo. According to an isothermal section of the Nb-Mo-NiAl system, Mo tends to occupy A-sites, although its diameter is smaller than Al, which prefers to occupy B-sites. These experimental observations indicate that there is no simple relationship between the Goldschmidt diameters and the site-substitution behavior of Al in the Laves phase. Edwards has pointed out the importance of the geometrical feature of Laves phases with site occupancy of the elements, and concluded that bcc metals tend to occupy A-sites, while fcc or hcp metals tend to occupy B-sites.³¹⁾ Thus, this rule seems to justify the occupancy of Al at B-sites in a number of Laves phases, although the Goldschmidt diameter of Al is large. However, bcc metals such as Cr and V substitute for B-site elements if the atomic diameters of the A-site elements are much larger than Cr or V.

To overcome this inconsistency, we should take into account that the size of Al atoms in some intermetallic compounds such as Ni₃Al and NiAl have been evaluated to be smaller than that of pure Al.³⁰⁾ Figure 6 shows the Al concentration dependence of the average atomic volumes of Ni-Al alloys and Nb(Ni,Al)₂ Laves phase. Figure 6(a) shows a way to evaluate the atomic volume of Al in the Ni solid

Table 2 Goldschmidt diameters $D_{C.N.12}$ of elements,³⁹⁾ together with the occupancy site in the NbCr₂ AB₂-Laves phase.

	Ni	Cr	V	Mo	Al	Nb	Ta
$D_{C.N.12}$ [nm]	0.249	0.257	0.270	0.280	0.286	0.294	0.294
Occupancy site	B-site	B-site	B-site	A-site	B-site	A-site	A-site

Fig. 6 Average atomic volumes ($\bar{V}$) of phases as a function of the atomic fraction of Al in the alloy composition. (a) Open circles: average atomic volumes of phases in the Ni-Al binary system, $\bar{V}_{Ni-Al}$ ³⁰⁾; closed triangles: average atomic volumes of the Nb(Ni,Al)₂-C14 phase in the Nb-Ni-Al ternary system, $\bar{V}_{Nb(Ni,Al)_2}$ ³⁷⁾. (b) Comparison of reported average atomic volumes for stoichiometric Nb(Ni,Al)₂ ($\bar{V}_{NbNiAl-3}$) with estimated atomic volumes. $\bar{V}_{NbNiAl-1}$ is a weighted average of V_{Nb} and $\bar{V}_{NiAl}$, and $\bar{V}_{NbNiAl-2}$ is an average of V_{Nb} , V_{Ni} , and V_{Al} .

solution V_{Al}' by extrapolating the line for Ni-rich $Ni_{1-x}Al_x$ to $Al = 100$ at%. It is clear that V_{Al}' is smaller than that of pure Al, V_{Al} . A considerable lattice contraction of Al has also been reported in fcc alloys, as shown in Table 3,^{30,38)} therefore, careful discussion is required to determine the atomic diameter of Al in alloys and compounds. In this study, Ni and Al in the $Nb(Cr,Ni,Al)_2$ or $Nb(V,Ni,Al)_2$ Laves phases are almost equiatomic and these elements occupy 2a and 6h sites with equal probability in stoichiometric $Nb(Ni,Al)_2$ ³⁷⁾; therefore, the average atomic diameter of Ni and Al is meaningful to examine the size factor effect on the stability of the Laves phases.

In Fig. 6, the average atomic volume $\bar{V}_{Ni(Al)}$, estimated from the extrapolated line of the Ni solid solution (C.N. 12) at $Al = 50$ at% is $11.8 \times 10^{-3} \text{ nm}^3$ (average atomic diameter of 0.261 nm).³⁰⁾ The C.N. 8 diameter $D_{B(Ni(Al)-obs)}$, is estimated by dividing the C.N. 12 average atomic diameter by 1.03, which is a widely accepted factor for the conversion of D (C.N. 12) to D (C.N. 8) based on the hypothesis that atomic volume does not change by allotropic transformation.³¹⁾ The evaluated $D_{B(Ni(Al)-obs)}$ (C.N. 8) is $0.261/1.03 = 0.248 \text{ nm}$, which is almost the same as the average atomic diameter of Ni and Al in $NiAl$ -B2, $D_{B(NiAl-obs)}$ (C.N. 8) = 0.249 nm. The reported average atomic volume of $Nb(Ni,Al)_2$ -C14 $\bar{V}_{NbNiAl-3}$, is consistent with the average volume of $\bar{V}_{NbNiAl-1}$ estimated as a weighted average of V_{Nb} and $\bar{V}_{NiAl}$, while it is smaller than the average atomic volume $\bar{V}_{NbNiAl-2}$, estimated from the average volumes of pure Nb, pure Ni, and pure Al. Thus, $\bar{V}_{NiAl}$ can be justified to examine the stability of Laves phases that contain the same amount of Ni and Al.

As the next step, $D_{B(X(Al)-obs)}$ (C.N. 8) and $D_{B(XAl-obs)}$ (C.N. 8) values in various X-Al binary systems at $Al = 50$ at% were estimated to examine the validity of applying the average atomic diameter estimated using the lattice constant of B2 aluminide, and are shown in Table 4 together with the estimated $D_{B(X/Al-obs)}$ (C.N. 8). While the difference between $D_{B(X(Al)-obs)}$ (C.N. 8) and $D_{B(X/Al-obs)}$ (C.N. 8) at $Al = 50$ at% in each binary system was larger than 0.008 nm (3.2%), the difference between $D_{B(X(Al)-obs)}$ (C.N. 8) and $D_{B(XAl-obs)}$ (C.N. 8) at $Al = 50$ at% in each binary system was within 0.003 nm (1.2%), which indicates that the average atomic diameter estimated from the average atomic volume of the fcc solid solution structure, $D_{B(X(Al)-obs)}$ (C.N. 8), is much closer to the diameter of B2 aluminide $D_{B(XAl-obs)}$

(C.N. 8) than $D_{B(X/Al-obs)}$ (C.N. 8). This means that the contraction of Al in the compound and solid solution alloys are almost the same, i.e., not sensitive to the crystal structure.

Now we should try the validity of the above discussion on the existence of AB_2 Laves phases composed of various combinations of pure A and XAl-B2 aluminide, or pure A and pure B.^{39–42)} (Table 5) Laves phases do not appear in the combination of A and B with D_A/D_B smaller than 1.05. In binary Laves phases, the most stable ratio of atomic diameter D_A/D_B is 1.225 and the reported ratio ranges between 1.05 and 1.68. As shown in Table 5, D_A/D_B among the A-(XAl) pseudo-binary systems is between 1.06 and 1.28, which is within the range observed in binary Laves phases. On the other hand, from application of D_B estimated from the average atomic volumes of the pure elements (X and Al) in B-sites, D_A/D_B of the $A(X,Al)_2$ Laves phase is evaluated to be between 0.96 and 1.17, which is out of the range for the binary Laves phase criterion. This indicates that estimation of D_B from the average atomic volumes of B2 aluminides is more suitable than that from the atomic volumes of pure elements. Here it should be noted that the VEC of Al-containing Laves phases shown in Table 5 is within 5.0–6.0, whereas those for a large amount of binary Laves phases are reported to be within 2.0–3.0 or 5.3–7.7.¹⁷⁾ According to the literature, Laves phases that contain Al exhibit rather low VECs, but almost within the stated range.

Further discussion based on the lattice geometry is required to examine the validity of the $D_{B(XAl-obs)}$ (C.N. 8) values estimated from B2 aluminides. Unless the atomic diameter ratio D_A/D_B is 1.225, A-site or B-site elements change their atomic size to minimize the total elastic energy in the Laves phase.²⁰⁾ The deviation of the estimated average atomic volume from the actual average atomic volume of the AB_2 Laves phase is defined as follows:

$$V_{Laves} = V_A + 2V_B + V_{AB} \quad (1)$$

where V_A and V_B are the atomic volumes of the A and B elements, respectively, and V_{AB} is the deviation. The CALPHAD method and first-principles calculations were applied to the binary C14 phase to determine the difference between the actual average atomic volume and the weighted average of the atomic volume of the pure elements.⁴³⁾ However, estimation of the interaction energy of Laves phase composed of all of the combinations of elements is difficult due to insufficient experimental information and a lack of first-principles calculations. Instead, the sizes of the

Table 3 Atomic diameters of Al in alloys estimated from extrapolated atomic diameter or average atomic volume of solid solution fcc phases, in the same manner as that with Fig. 6(a).

Alloys	Extrapolated atomic diameter of Al [nm]
Co-Al	0.263 ³⁰⁾
Rh-Al	0.269 ³⁰⁾
Ir-Al	0.267 ³⁰⁾
Ni-Al	0.262 ³⁰⁾
Pd-Al	0.264 ³⁰⁾
Pt-Al	0.264 ³⁰⁾
Cu-Al	0.272, ³⁰⁾ 0.271 ³⁸⁾
Ag-Al	0.280, ³⁰⁾ 0.2799–0.2808 ³⁸⁾
Au-Al	0.277, ³⁰⁾ 0.277 ³⁸⁾

Table 4 Average atomic diameters of X-50Al (C.N. 8) as a B2 structure ($D_{B(XAl-obs)}$), the values estimated from those of the fcc structure ($D_{B(X(Al)-obs)}$) and the average values of the atomic diameters of pure elements ($D_{B(X/Al-obs)}$) [nm].

	NiAl	CoAl	PdAl	RhAl	IrAl
$D_{B(XAl-obs)}$	0.249	0.248	0.264	0.258	0.258
$D_{B(X(Al)-obs)}$	0.248	0.249	0.262	0.261	0.261
Difference	0.001	–0.001	0.002	–0.003	–0.003
$(D_{B(XAl-obs)} - D_{B(X(Al)-obs)})$	(0.5%)	(–0.4%)	(0.8%)	(–1.1%)	(–1.2%)
$D_{B(X/Al-obs)}$	0.260	0.2605	0.2725	0.2695	0.2705
Difference	–0.011	–0.013	–0.008	–0.011	–0.013
$(D_{B(XAl-obs)} - D_{B(X/Al-obs)})$	(–4.3%)	(–5.1%)	(–3.2%)	(–4.4%)	(–4.9%)

Table 5 Existence of Laves phase with respect to combinations of A and B with the ratio of average atomic diameter D_A/D_B and the VEC given in parentheses.³⁹⁻⁴²⁾ 'No phase diagram' means there is no information regarding the equiatomic composition of the three elements.

A \ B	CoAl	NiAl	Cr	FeAl	RhAl	IrAl	RuAl	V	PdAl	PtAl	Mo	ScAl	D_A/D_B (VEC)
Cr	1.01 (6.0)	1.00 (6.3)	-	0.99 (5.7)	0.97 (6.0)	0.97 (6.0)	0.96 (5.7)	0.95 (5.3)	0.95 (6.3)	0.94 (6.3)	0.92 (6.0)	0.84 (4.0)	
V	1.06 (5.7)	1.05 (6.0)	1.05 (5.7)	1.04 (5.3)	1.02 (5.7)	1.01 (5.7)	1.01 (5.3)	-	0.99 (6.0)	0.98 (6.0)	0.96 (5.7)	0.88 (3.7)	
Mo	1.10 (6.0)	1.09 (6.3)	1.09 (6.0)	1.08 (5.7)	1.06 (6.0)	1.05 (6.0)	1.05 (5.7)	1.04 (5.3)	1.03 (6.3)	1.02 (6.3)	-	0.92 (4.0)	
W	1.10 (6.0)	1.10 (6.3)	1.10 (6.0)	1.09 (5.7)	1.06 (6.0)	1.06 (6.0)	1.05 (5.7)	1.05 (5.3)	1.04 (6.3)	1.03 (6.3)	1.01 (6.0)	0.92 (4.0)	
Nb	1.15 (5.7)	1.15 (6.0)	1.14 (5.7)	1.13 (5.3)	1.11 (5.7)	1.11 (5.7)	1.10 (5.3)	1.09 (5.0)	1.08 (6.0)	1.07 (6.0)	1.05 (5.7)	0.96 (3.7)	
Ta	1.15 (5.7)	1.15 (6.0)	1.14 (5.7)	1.13 (5.3)	1.11 (5.7)	1.11 (5.7)	1.10 (5.3)	1.09 (5.0)	1.08 (6.0)	1.07 (6.0)	1.05 (5.7)	0.96 (3.7)	
Ti	1.17 (5.3)	1.16 (5.7)	1.16 (5.3)	1.15 (5.0)	1.12 (5.3)	1.12 (5.3)	1.11 (5.0)	1.11 (4.7)	1.10 (5.7)	1.09 (5.7)	1.06 (5.3)	0.97 (3.3)	
Hf	1.26 (5.3)	1.25 (5.7)	1.25 (5.3)	1.24 (5.0)	1.21 (5.3)	1.21 (5.3)	1.20 (5.0)	1.19 (4.7)	1.18 (5.7)	1.17 (5.7)	1.15 (5.3)	1.05 (3.3)	
Zr	1.28 (5.3)	1.27 (5.7)	1.27 (5.3)	1.26 (5.0)	1.23 (5.3)	1.23 (5.3)	1.22 (5.0)	1.21 (4.7)	1.20 (5.7)	1.19 (5.7)	1.17 (5.3)	1.07 (3.3)	

No Laves

Stoichiometric Laves

Non-stoichiometric Laves

No phase diagram

component atoms in multi-component Laves phase are evaluated based on geometrical explanations for the contraction and expansion of the constituent atoms. According to Edwards,³¹⁾ when a stacking structure of Laves phase is visualized by mutual stacking of an A metal layer and a B metal layer, the mean closest distances of A-A, $d_{A(g)}$, and B-B, $d_{B(g)}$, are expressed as functions of D_A (C.N. 8) and D_B (C.N. 12).

$$d_{A(g)} = \frac{4D_A(\text{C.N.8}) + 9.8D_B(\text{C.N.12})}{12} \quad (2)$$

$$d_{B(g)} = \frac{4D_A(\text{C.N.8}) + 9.8D_B(\text{C.N.12})}{14.7} \quad (3)$$

Equations (2) and (3) can respectively be rewritten in the lat-

tice contraction forms.

$$\frac{D_A(\text{C.N.8})}{d_{A(g)}} = \frac{12 \times (D_A(\text{C.N.8})/D_B(\text{C.N.12}))}{4 \times (D_A(\text{C.N.8})/D_B(\text{C.N.12})) + 9.8} \quad (4)$$

$$\frac{D_B(\text{C.N.12})}{d_{B(g)}} = \frac{14.7}{4 \times (D_A(\text{C.N.8})/D_B(\text{C.N.12})) + 9.8} \quad (5)$$

When D_A/D_B is an ideal Laves phase value of 1.225, both $D_A/d_{A(g)}$ and $D_B/d_{B(g)}$ are unity, and each element in the Laves phase neither expands nor contracts. $D_A/d_{A(g)}$ greater than unity indicates contractions of the A atoms in the Laves phase, while $D_A/d_{A(g)}$ less than unity indicates expansion.

Most of the Laves phases do not have an ideal D_A/D_B ; therefore, the distance of B-B has several variations because there are two types of sites for B elements, 2a and 6h.

Therefore, the distance of B-B, $d_{B(\text{obs})}$, should be estimated as a weighted average of the 2a-6h and 6h-6h distances (no first-nearest-neighbor relationship between atoms that both occupy 2a sites). A broad survey of the atomic positions in various Laves phases enables the experimentally determined mean closest distances of A-A, $d_{A(\text{obs})}$, and B-B, $d_{B(\text{obs})}$, to be evaluated. Evaluation of $d_{A(\text{obs})}$ and $d_{B(\text{obs})}$ is conducted with stoichiometric $A(X,Al)_2$ ternary Laves phases (X: elements forming B2 compounds with Al, such as Ni, Co, Fe, Ir, and Rh) shown in Table 5 as 'Stoichiometric Laves' to verify the use of $D_{B(XAl\text{-obs})}$ (C.N. 8) estimated from the lattice constant of B2 aluminides, instead of D_B (C.N. 8) estimated by averaging the Goldschmidt radii of elements that occupy B-sites by comparison of D_A/d_A and D_B/d_B with $D_A/d_{A(g)}$ and $D_B/d_{B(g)}$ estimated using eqs. (4) and (5).³⁹⁾

Figure 7 shows the results of the comparison. Two types of $D_A/d_{A(\text{obs})}$ and $D_B/d_{B(\text{obs})}$ are plotted against D_A/D_B . The curves show the lattice contraction based on the geometrical model, $D_A/d_{A(g)}$ and $D_B/d_{B(g)}$ estimated from eqs. (4) and (5), respectively, and the actual contraction $D/d_{(\text{obs})}$, can be compared by plotting against the ratio of the average atomic diameter, D_A/D_B . For various stoichiometric $A(X,Al)_2$ ternary Laves phases, the adequacy of using the average atomic diameter of $XAl\text{-B2}$ $D_{B(XAl\text{-obs})}$, as the D_B value was tested by comparison with that using the average atomic diameter of pure X and pure Al, $D_{B(X/Al\text{-obs})}$. The triangle symbols represent the values using $D_B = D_{B(X/Al\text{-obs})}$, which are greater than the curves using $D_A/d_{A(g)}$ and $D_B/d_{B(g)}$ obtained from the geometrical model, whereas the circle symbols represent the values using the D_B value estimated as $D_{B(XAl\text{-obs})}$, which shows good agreement with the curves. Therefore, the geometrical properties of a Laves phase composed of equi-atomic X and Al could be argued using the D_B value estimated from the average atomic diameters of B2 in the A-X-Al system.

In terms of the elements that occupy B-sites in the Laves phases in the Nb-Cr-NiAl and Nb-V-NiAl systems, let us compare D_B for NiAl-B2, a highly ordered bcc compound, and D_B for the bcc elements Cr and V (Fig. 8). The atomic diameter of Cr is as small as that of NiAl-B2, which may result in a substitution of Cr on B-sites in $Nb(Ni,Al)_2$, as confirmed by the direction of the solubility lobe of the Laves phase in Nb-Cr-NiAl (Fig. 5(a)). Moreover, the constant $D_A/$

D_B , regardless of Cr substitution for B-sites of the $Nb(Ni,Al)_2$ Laves phase is considered to maintain the stability sufficiently high to appear as a stable phase. In the case of the Nb-V-NiAl system, there are two conceivable substitution or defect behaviors that cause the direction of the solubility lobe of the C14 phase to be only slightly deviated toward the V corner from the Nb-constant line (Fig. 5(b)). One is the occurrence of vacancies in A-sites and V substitution for B-sites in $Nb(Ni,Al)_2\text{-C14}$. The other is V substitution for both A-sites and B-sites in $Nb(Ni,Al)_2\text{-C14}$. The latter is a more likely explanation because, according to Stein *et al.*,¹⁷⁾ reported defects that exist in non-stoichiometric Laves phases are anti-site substitution of either site, or vacancies of B-sites, but not vacancies in A-sites. The atomic diameter of V, which is between that of NiAl-B2 and Nb, may be the reason why V substitutes for both sites in $Nb(Ni,Al)_2\text{-C14}$. On the other hand, the reported Nb-Mo-NiAl isothermal section shows the preferential substitution of Mo on A-sites in $Nb(Ni,Al)_2\text{-C14}$ ¹⁶⁾ because the diameter of Mo is larger than that of V. Similar relationships between the site occupancy behavior in the $Ta(Ni,Al)_2$ Laves phase and the diameters of additional elements (Cr, V and Mo) have been found in Ta-Cr-NiAl, Ta-V-NiAl, and Ta-Mo-NiAl isothermal sections. It can be concluded that the tendency of the site occupancy can be explained not only for ternary Laves phases but also for quaternary Laves phases that include Ni and Al, by taking the average atomic size of NiAl-B2 into account.

In this study, the site-substitution behavior of Cr, V, and Mo in the $Nb(Ni,Al)_2\text{-C14}$ phase and the phase stability could be argued by comparison of the average atomic diam-

Fig. 8 Average atomic diameters of bcc elements (C.N. 8) and NiAl (C.N. 8) estimated from the lattice constant a of each element. $D(\text{C.N. 8}) = a\sqrt{3}/2$.

Fig. 7 Lattice contractions D/d as a function of the ratio of average atomic diameters D_A/D_B in Laves phases in terms of (a) A-site elements and (b) B-site elements. Circles: average atomic diameters in B2 compounds, $D_{B(XAl\text{-obs})}$ as D_B . Triangles: average atomic diameters in pure X and Al elements, $D_{B(X/Al\text{-obs})}$ as D_B . Curves represent $D/d_{(g)}$ obtained from the geometrical model proposed by Edwards.³¹⁾

eter of NiAl-B2 and the atomic diameters of Cr, V, and Mo, based on the substitution of Ni and Al for 2a and 6h sites with equal probability in the stoichiometric Nb(Ni,Al)₂-C14 phase. However, because the site preference of Ni and Al for 2a and 6h sites is composition-dependent, the Nb(Ni,Al)₂-C14 phase with a non-equiatom composition of Ni and Al does not have equal probability of substitution for them at each site, which indicates that further consideration is required for evaluation of the size factor in non-stoichiometric C14 phases.³⁷⁾

5. Concluding Remarks

The phase equilibria among bcc_{ss}/B2/C14 in the Nb-Cr-NiAl and the Nb-V-NiAl sections of the quaternary systems were investigated. In the Nb-Cr-NiAl system, the direction of the solubility lobe of the C14 phase extends along a line of Nb(Ni,Al)₂-NbCr₂. On the other hand, in the Nb-V-NiAl system, the solubility lobe of the C14 phase deviates slightly toward the V corner from the line connecting Nb(Ni,Al)₂ and hypothetical "NbV₂". These solubility lobes could be explained by comparison of the average atomic diameters of NiAl-B2, Cr and V, which was confirmed by the geometrical model proposed by Edwards.³¹⁾ The similarity of the average atomic diameter of NiAl and the diameter of Cr explains the site-substitution behavior of Cr for Nb(Ni,Al)₂-C14. The diameter of V is rather larger than the average diameter of NiAl but smaller than Nb; therefore, V substitutes not only on B-sites but also on A-sites. These experimental results together with information on other reported ternary Laves phases strongly suggests that the average atomic size of elements that occupy B-sites such as Ni and Al in Nb(Ni,Al)₂ Laves phase should be estimated from the lattice constant of the B2 phase composed of B-site-occupying elements such as NiAl.

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Nomenclature

$R_{C.N.12}$	Goldschmidt radius (nm)
$D_{C.N.12}$	Goldschmidt diameter (nm)
$D_A(C.N.8)$	atomic diameter (C.N. 8) of pure A (nm)
$D_B(C.N.12)$	atomic diameter (C.N. 12) of pure B (nm)
$d_{A(g)}$	mean closest distance of A-A in Laves phase from the geometrical model by Edwards (nm)
$d_{A(obs)}$	mean closest distance of A-A in Laves phase from Pearson's Crystal Data (nm)
$d_{B(g)}$	mean closest distance of B-B in Laves phase

$d_{B(obs)}$	from the geometrical model by Edwards (nm)
V_{Laves}	mean closest distance of B-B in Laves phase from Pearson's Crystal Data (nm)
V_A	average atomic volume of Laves phase (nm ³)
V_B	atomic volume of pure A (nm ³)
V_{AB}	atomic volume of pure B (nm ³)
V_{Al}'	difference between V_{Laves} and $(V_A + 2V_B)$ (nm ³)
V_{Al}	atomic volume of Al in Ni solid solution (nm ³)
$\bar{V}_{Ni(Al)}$	atomic volume of pure Al (nm ³)
$\bar{V}_{NiAl}$	average atomic volume of Ni _{0.5} Al _{0.5} on an extrapolated line of Ni _{1-x} Al _x (nm ³)
$D_{B(Ni(Al)-obs)}$	average atomic volume of NiAl-B2 (nm ³)
$D_{B(X(Al)-obs)}$	average atomic diameter of Ni _{0.5} Al _{0.5} estimated from $\bar{V}_{Ni(Al)}$ (nm)
$\bar{V}_{NbNiAl-1}$	average atomic diameter of X _{0.5} Al _{0.5} estimated from $\bar{V}_{X(Al)}$ (nm)
$\bar{V}_{NbNiAl-2}$	average atomic diameter of NiAl-B2 (nm)
$\bar{V}_{NbNiAl-3}$	average atomic diameter of XAl-B2 (nm)
	average atomic diameter of pure X and pure Al (nm)
	weighted average atomic volume of pure Nb and NiAl-B2 $((V_{Nb} + 2\bar{V}_{NiAl})/3)$ (nm ³)
	average atomic volume of pure Nb, pure Ni and pure Al $((V_{Nb} + V_{Ni} + V_{Al})/3)$ (nm ³)
	experimental average atomic volume of stoichiometric Nb(Ni,Al) ₂ -C14 (nm ³)

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