Effect of Si Addition on Microstructure and Mechanical Properties of Dual Two-Phase Ni₃Al and Ni₃V Intermetallic Alloys

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The effects of Si addition on the microstructures and mechanical properties of dual two-phase Ni₃Al and Ni₃V intermetallic alloys with a composition of Ni₇₅Al₉V₁₃Nb₃ (expressed by at%) were investigated, focusing on the substitution manner of Si for Ni, Al or V. Solubility limit of Si in the present microstructure was less than 2 at% Si irrespective of the substitution manner of Si for Ni, Al or V. The eutectoid microstructure in the channel region was degenerated when Si was substituted for V. Third-phase dispersions containing Nb, i.e., Ni₁₆Si₇Nb₆ (G phase: D8a) were present at grain boundaries of the alloys exceeding the solubility limit. In the alloy in which Si was substituted for Ni, unit cell volume of the constituent Ni₃Al phase increased while that of the constituent Ni₃V phase little changed. In the alloy in which Si was substituted for Al, unit cell volumes of both phases decreased. The alloys in which Si was substituted for Al or Ni hardened while the alloy in which Si was substituted for V softened. The hardening in the former alloys was attributed to solid solution hardening due to Si substituted for solvent atoms Ni, Al and/or V while the softening in the latter alloy was attributed to the degenerated eutectoid microstructure in the channel region. Also, it was shown that the third-phase dispersions little affected hardness as well as yield strength. [doi:10.2320/matertrans.M2015436]

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1. Introduction

Ni₃X-type intermetallic alloys exhibit high phase and microstructural stabilities because of low atomic diffusivity owing to their geometrically close packed (GCP) structures.^{1–4)} However, monolithic Ni₃X-type intermetallic alloys have some drawbacks, poor ductility at room temperature, low creep strength at high temperature and so on. So-called Ni-based dual two-phase intermetallic alloys^{5–13)} based on Ni₃Al (L1₂: $a = 0.3572$ nm) - Ni₃V (D0₂₂: $a = 0.3542$ nm and $c/a = 2.036$) pseudo-binary alloy system (Fig. 1)¹⁴⁾ have a unique microstructure: the alloys with a hypereutectoid alloy composition exhibit a mono-phase microstructure of Ni solid solution (A1 phase) at temperatures below melting point and subsequently a two-phase microstructure of the cuboidal Ni₃Al phase surrounded by the A1 phase with decreasing temperature. Accordingly, the microstructure at high temperatures is quite same as that observed in conventional Ni base γ (A1)/ γ' (L1₂)-type superalloys in which the cuboidal γ' phase with a larger volume fraction is surrounded by the channel region consisting of the γ phase with a smaller volume fraction. At further low temperature, the A1 phase remained in the channel region is transformed to a lamellar-like microstructure consisting of the Ni₃Al and Ni₃V phases by the eutectoid reaction at 1281 K. Crystal structures of A1, L1₂ and D0₂₂ relating to the formation of the dual two-phase Ni₃Al and Ni₃V microstructure are shown in Fig. 2. The dual two-phase microstructures are highly coherent among the constituent phases (structures), and display high microstructural stability.^{5,6,8,9)} In addition, high-temperature mechanical properties (such as tensile and creep strength) of the Ni-based dual two-phase intermetallic alloys were superior to those of many conventional superalloys.^{7,9)}

Further improving the Ni-based dual two-phase intermetallic alloys is necessary to develop as next generation-type high temperature structural materials. As one of this strategy, add-

Fig. 1 Phase diagram of the Ni₃V-Ni₃Al pseudo-binary alloy system.¹⁴⁾ Note that the hypereutectoid alloy compositions have been used for the development of so-called dual two-phase Ni₃Al-Ni₃V intermetallic alloys.

Fig. 2 Crystal structures of (a) A1 (fcc), (b) L1₂ (Ni₃Al) and (c) D0₂₂ (Ni₃V).

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ing some alloying elements to the Ni-based dual two-phase intermetallic alloys has been attempted. Ti^{7,9)} and Nb^{11–13)} resulting in solid solution strengthening have been so far added, and also boron^{7,11,13)} improving tensile elongation has been doped. Si which would be a useful element for application to aero components has also been added to the Ni-based dual two-phase intermetallic alloys, and was shown to actually improve oxidation resistance and decrease density, as expected.¹⁵⁾ For alloying behavior of Si in the Ni-based dual two-phase microstructure, it has been observed that Si is more soluble in Al phase than two intermetallic constituent phases.¹⁶⁾ Alloying behavior of Si in Ni₃Al phase is well known: Si is much soluble, substituting for Al.¹⁷⁾ However, that of Si in Ni₃V phase is not well known although thermodynamic calculation predicts the substitution of Si for Ni rather than for V.¹⁸⁾ Thus, the effect of Si on the microstructure as well as the mechanical properties of the Ni-based dual two-phase intermetallic alloys has not been well clarified. Therefore, in this study, we investigate in detail the microstructures and room-temperature mechanical properties such as hardness and tensile properties. The microstructures and mechanical properties of the Si-added Ni-based dual two-phase intermetallic alloys are studied particularly focusing on the effect of the substitution manner of Si for Ni, Al or V.

2. Experimental Procedures

Alloys used in this study were prepared from starting raw materials of 99.99 wt% Ni, 99.99 wt% Al, 99.9 wt% V, 99.9 wt% Nb, 99.999 wt% Si and 99.8 wt% boron (B). Alloy button ingots with a diameter of 30 mm were made by arc melting in an argon gas atmosphere using a non-consumable tungsten electrode on a copper hearth. Each alloy button was remelted at least three times to ensure chemical homogeneity through an entire cross section of button. The weight loss of the button ingots after arc melting was mostly less than 0.2%, therefore indicating that the designed alloy compositions were prepared.

A base alloy composition used in this study is Ni₇₅Al₉V₁₃Nb₃ (formulated by at%) doped with 50 wt. ppm B, as shown in Table 1. The reason why Nb is contained in the base alloy composition is that Nb is expected to enhance high-temperature strength^{11–13)} through stabilizing two constituent phases Ni₃Al and Ni₃V, and also acting as solid solution strengthener in them.¹⁵⁾ A small amount of B was doped to suppress grain boundary fracture of the alloys.^{7,11,12)} Si was added at two different levels of 1 and 2 at% to the base alloy composition, substituting either for Ni, Al or V. Hereafter, these alloy compositions are referred to as base, 1Si(Ni), 1Si(Al), 1Si(V), 2Si(Ni), 2Si(Al) and 2Si(V) alloys. Alphabet in the parenthesis means species for which Si is substituted. The alloy button ingots were homogenized at 1553 K for 5 h in a vacuum and then furnace-cooled to room temperature at a cooling rate of approximately 10 K/min. They were then sliced to sizes suitable for specimens used in following experiments, using an electron discharge machine (EDM).

Microstructures of the prepared alloys were investigated by a field emission-type scanning electron microscope (FE-SEM: JSM-7001F operating at 15 kV) and an electron probe micro analyzer (EPMA: JXA-8530F equipped with WDS

Table 1 Chemical compositions of the alloys used in this study.

Alloys ^a	Ni	Al	V	Nb	Si	B ^b
	(at%)					(wtppm)
Base	75	9	13	3	-	50
1Si(Ni)	74	9	13	3	1	50
1Si(Al)	75	8	13	3	1	50
1Si(V)	75	9	12	3	1	50
2Si(Ni)	73	9	13	3	2	50
2Si(Al)	75	7	13	3	2	50
2Si(V)	75	9	11	3	2	50

^a Alphabet in the parenthesis means species for which Si was substituted.

^b The content of B is not included in the total.

(wave dispersive spectroscopy) operating at 15 kV). The sliced specimens were mechanically abraded on SiC paper and then electrolytically polished in a mixture solution of 15 vol.% H₂SO₄ + 85 vol.% CH₃OH at 263 K. Also, X-ray diffraction (XRD: RINT2500) measurements were performed using Ni-filtrated CuK α radiation at an accelerated voltage of 40 kV. The diffraction profiles for identifying the constituent phases were drawn at a scanning speed of 1°/min in diffraction angle range between 2 θ = 20° and 100°. On the other hand, those for measuring the lattice parameters of two constituent phases were drawn at a scanning speed of 0.1°/min in diffraction angle range between 2 θ = 72° and 78°. In this diffraction angle range, three {220} reflection peaks have to appear at very close diffraction angle intervals; (220) reflection peak from the Ni₃Al phase at near 2 θ = 75.17°, and (220) and (204) reflection peaks from the Ni₃V phase at near 2 θ = 75.96° and 2 θ = 75.11°, respectively. The lattice parameters *a* of the Ni₃Al phase were calculated using the (220) reflection peak. The lattice parameters *a* and *c* of the Ni₃V phase were calculated using the (220) and (204) reflection peaks, respectively, according to a following equation:

$$1/d^2 = 4 \sin^2 \theta / \lambda^2 = (h^2 + k^2)/a^2 + l^2/c^2, \quad (1)$$

where *d* is interplanar spacing, θ is diffraction angle, λ is a wave-length of X-ray, *a* and *c* are lattice parameters, and *h*, *k* and *l* are Miller indices.

Mechanical properties were evaluated by Vickers hardness test and tensile test at room temperature. The Vickers hardness test was conducted with a holding time of 10 s and a load of 1 kg. Hardness data points more than 10 were collected and averaged in each experimental condition. For the tensile test, specimens with a gauge dimension of 2 × 1 × 10 mm³ were cut from the homogenized arc buttons using EDM. The tensile axis of the tensile specimen was chosen to be perpendicular to solidification direction of the arc-melted buttons. The tensile specimens were deformed at an initial strain rate of 1.66 × 10⁻⁴ s⁻¹ up to fracturing. The tensile yield strength defined at 0.2% plastic strain and tensile elongation defined by plastic strain to fracture were calculated from load–elongation curves drawn on the charts.

3. Results

3.1 Microstructural observation by SEM and EPMA

Figure 3 shows SEM-BEIs (back scattered electron imag-

Fig. 3 SEM-BEIs of the microstructures of the (a) base, (b) 1Si(Ni), (c) 1Si(Al), (d) 1Si(V), (e) 2Si(Ni), (f) 2Si(Al) and (g) 2Si(V) alloys observed at a low magnification.

es) of the microstructures of the alloys observed at a low magnification. The microstructures of all the alloys were composed of grains with a size of a few hundred μm . Grain interior showed featureless microstructure. In the 2Si(Ni), 2Si(Al) and 2Si(V) alloys, some third-phase dispersions with a length of several μm were observed along grain boundaries, indicating that solubility limit of Si in the present dual two-phase microstructure is small, less than 2 at% Si.

SEM-SEIs (secondary electron images) of the microstructures in the grain interior (matrix) of the alloys observed at a high magnification are shown in Fig. 4. In all the alloys, the two-phase microstructure consisting of primary Ni_3Al precipitates and channel region is clearly observed. In the channel regions, so-called secondary Ni_3Al precipitates were mostly present in precipitation form. Except for the secondary Ni_3Al precipitates, it is however impossible to fully resolve the eutectoid microstructure in the channel region by SEM observation. The previous observation by TEM indicates that the channel regions are composed of the eutectoid microstructure consisting of Ni_3V and Ni_3Al .^{12,13,19)} The size and morphology of the primary Ni_3Al precipitates are not so different among all the alloys, in other words, similar irrespective of Si content or the substitution manner of Si for Ni, Al or V. However, the size of the primary Ni_3Al precipitates of the 2Si(Ni) and 2Si(V) alloys appears to be slightly larger than that of the base alloy, while that of the 2Si(Al) alloy appears to be slightly smaller than that of the base alloy.

Elemental distributions in the microstructures of the 2Si(Ni), 2Si(Al) and 2Si(V) alloys which exceeded their solubility limits were investigated. Figure 5 shows SEM-BEI and elemental distributions in the microstructure of the

2Si(Ni) alloy. Also, Table 2 shows alloy compositions analyzed in the matrix, i.e., grain interior (marked by position 1) and third-phase dispersions (marked by position 2) of the 2Si(Ni) alloy. The former position was analyzed with a relatively large probe diameter to obtain average composition over the grain interior while the latter position was analyzed with a probe diameter as small as possible to obtain chemical composition in a confined area. It is evident from Table 2 that the alloy composition in the grain interior (marked by the position 1) is well identical to the nominal composition (i.e., the overall composition) of the 2Si(Ni) alloy. The dual two-phase microstructure developed in the grain interior is well resolved by the pattern of the elemental distribution where Al is enriched in the primary Ni_3Al precipitates and V is enriched in the channel region. Si appears to be enriched in the channel region, as understood from the fact that the elemental distribution of Si is similar to that of V. The partition behavior of Si in Fig. 5 is consistent with the previous observation: Si was found to be more soluble in the prior Ni solid solution (A1 phase), i.e. the channel region than in the Ni_3Al phase.¹⁶⁾ It was also found that the third-phase dispersions at grain boundaries were composed of Nb, Si and a low content of Ni, whose chemical composition is close to $\text{Ni}_{16}\text{Si}_7\text{Nb}_6$ (G phase: D8a) identified by the following XRD measurement (Fig. 6e). Same kind of dispersions were also observed in the 2Si(Al) alloy as well as the 2Si(V) alloy.

3.2 Structural observation by XRD

Figure 6 shows X-ray diffraction patterns of the alloys studied in this study. In the base, 1Si(Ni), 1Si(Al) and 1Si(V) alloys, all reflection peaks were indexed as the Ni_3Al and

Fig. 4 SEM-SEIs of microstructures of the (a) base, (b) 1Si(Ni), (c) 1Si(Al), (d) 1Si(V), (e) 2Si(Ni), (f) 2Si(Al) and (g) 2Si(V) alloys observed at a high magnification.

Fig. 5 SEM-BEI and elemental distributions of Ni, Al, V, Nb and Si in the microstructure of the 2Si(Ni) alloy. In the SEM-BEI, alloy compositions in the grain interior and third-phase dispersions at grain boundaries were measured in a position "1" encircled and in a position "2", respectively, and their values are shown in Table 2.

Ni_3V phases. In the 2Si(Ni) and 2Si(V) alloys, additional reflection peaks indexed as $\text{Ni}_{16}\text{Si}_7\text{Nb}_6$ (G phase) were observed, whose chemical composition is almost identical to that deduced from the third-phase dispersions observed by the EPMA (Fig. 5). In the 2Si(Al) alloy, any additional reflection peaks were not observed probably because of small volume fraction of the third-phase dispersions. These XRD results are consistent with the SEM and EPMA results observed

in Figs. 3–5.

Figure 7 shows XRD profiles at diffraction angle corresponding to {220} reflections of the base, 1Si(Ni), 1Si(Al) and 1Si(V) alloys. The reflection profiles of the base, 1Si(Ni) and 1Si(Al) alloys are not separated to three peaks but separated to two peaks. This is because the (220) reflection peak from the Ni_3Al phase and the (204) reflection peak from the Ni_3V phase are overlapped. However, it is demonstrated from the

Table 2 Alloy compositions (at%) analyzed in the matrix (grain interior) and third-phase dispersions of the 2Si(Ni) alloy.

Element	Nominal composition of alloy	Position 1 (matrix)	Position 2 (dispersion)
Ni	73	73.5	58.8
Al	9	8.9	1.6
V	13	13.8	3.1
Nb	3	1.9	14.3
Si	2	0.4	22.2

Fig. 6 XRD profiles of the (a) base, (b) 1Si(Ni), (c) 1Si(Al), (d) 1Si(V), (e) 2Si(Ni), (f) 2Si(Al) and (g) 2Si(V) alloys.

figures that the eutectoid microstructure consisting of ($\text{Ni}_3\text{Al} + \text{Ni}_3\text{V}$) is certainly formed in the channel region of the base, 1Si(Ni) and 1Si(Al) alloys. On the other hand, the reflection profile of the 1Si(V) alloy is separated to neither three peaks nor two peaks, suggesting that the eutectoid microstructure is not sufficiently formed in the 1Si(V) alloy.

Lattice parameters and unit cell volumes were measured to evaluate lattice property of Si that is soluble in the two intermetallic phases using the {220} reflections shown in Fig. 7, and plotted in Fig. 8. Here, c axes and unit cell volumes V of the Ni_3V phase were divided by a factor 2 and plotted to equivalently compare with those of the Ni_3Al phase. The data for the 1Si(V) alloy was not plotted in these figures because the {220} reflection peaks from the two intermetallic phases were not well separated, as described earlier (Fig. 7). Here, we have to keep it in mind that the data points are plotted on the horizontal axis scaled by the nominal (i.e., overall) Si content in the alloy but not plotted on that scaled by the Si

Fig. 7 XRD profiles at diffraction angle ($2\theta \sim 75^\circ$) corresponding to {220} reflections of the base, 1Si(Ni), 1Si(Al) and 1Si(V) alloys.

content which is actually partitioned in the two intermetallic phases of the alloys. If estimating the partition of Si to the two intermetallic phases in this base alloy,¹⁶⁾ the data points for the Ni_3Al phase may be plotted at higher Si contents than 1 at% while those for the Ni_3V phase at lower Si contents than 1 at%.

Distinctive lattice properties of Si soluble in the two intermetallic phases were observed between the 1Si(Ni) and 1Si(Al) alloys. First, looking at the Ni_3Al phase, a axis for the 1Si(Ni) alloy increased while that for the 1Si(Al) alloy decreased (Fig. 8a). Correspondingly, the unit cell volume V for the 1Si(Ni) alloy increased while that for the 1Si(Al) alloy decreased (Fig. 8c). Assuming that atomic radii of Ni, Al, V and Si are 0.125, 0.143, 0.140 and 0.131 nm, respectively (where Goldschmidt radius is given for the latter two atoms with non-close packed structures (coordination number (Z) $\neq 12$), it is suggested that the majority of Si is substituted for Ni (with a smaller atomic radius than Si) in the case of the 1Si(Ni) alloy while the majority of Si is substituted for Al (with a larger atomic radius than Si) in the case of the 1Si(Al) alloy. Next, looking at the Ni_3V phase, a axes decreased and c axes increased for the 1Si(Ni) alloy as well as the 1Si(Al) alloy (Fig. 8b). To evaluate the effect of Si addition on structural tetragonality of the constituent Ni_3V phase, axial ratio defined by $(c/2)/a$ was calculated using Fig. 8b and plotted in Fig. 9. Consequently, it was found that the structural tetragonality is enhanced by the addition of Si and more enhanced when Si is substituted for Al than for Ni. Regarding the unit cell volumes of the Ni_3V phase, that in the 1Si(Ni) alloy little changed while that in the 1Si(Al) alloy substantially decreased. In the case of the 1Si(Al) alloy, it is suggested that the majority of Si partitioned into the Ni_3V phase was substituted for V (with a larger atomic radius than Si). In the case of the 1Si(Ni) alloy, it appears that a certain portion of Si were substituted for V instead of Ni. Consequently, it is considered that substantial increase in the unit cell volume of the Ni_3V phase did not take place.

Fig. 8 Lattice parameters (a, b) and unit cell volumes (c, d) of the Ni₃Al (a, c) and Ni₃V (b, d) phases in the base, 1Si(Ni) and 1Si(Al) alloys. The lattice parameters of c axis and unit cell volumes V of the Ni₃V phase were divided by a factor 2 and plotted to compare with those of the Ni₃Al phase.

Fig. 9 Axial ratio $(c/2)/a$ of the base, 1Si(Ni) and 1Si(Al) alloys.

Fig. 10 Vickers hardness of the base, Si(Ni), Si(Al) and Si(V) alloys.

3.3 Mechanical properties

Figure 10 shows Vickers hardness of the base, Si(Ni), Si(Al) and Si(V) alloys. Looking at the alloys with 1 at% Si below the solubility limit, hardness of the 1Si(Al) and 1Si(Ni) alloys increased: the former alloy more hardened than the latter alloy. Contrarily, the hardness of the 1Si(V) alloy substantially decreased: the 1Si(V) alloy softened. Thus, the hardness depends on the substitution manner of Si for Ni, Al or V, and is ranked as $\text{Si(Al)} > \text{Si(Ni)} > \text{Si(V)}$. For the alloys with 2 at% Si beyond the solubility limit, it appears that the hardness of all the alloys is little enhanced by the third-phase dispersions, meaning that they do not contribute to hardening of the alloys.

Figure 11 shows yield strength $\sigma_{0.2}$ and tensile elongation ϵ_f of the base, Si(Ni), Si(Al) and Si(V) alloys. Looking at the

alloys below the solubility limit, the yield strength of the 1Si(Al) and 1Si(Ni) alloys increased: the former alloy more strengthened than the latter alloy. Contrarily, the 1Si(V) alloy decreased: the 1Si(V) alloy softened. Thus, the yield strength again depends on the substitution manner of Si for Ni, Al or V, and is ranked as $\text{Si(Al)} > \text{Si(Ni)} > \text{Si(V)}$. For the alloys beyond the solubility limit, the yield strength of all the alloys is little enhanced by the third-phase dispersions, indicating that they little contributed to the strengthening of the alloys. Thus, the behavior of the hardness is similar to that of the Vickers hardness. On the other hand, the tensile elongation of all the alloys decreased, meaning that the soluble Si as well as the third-phase dispersions is not beneficial to the tensile elongation of the alloys. It is here noted that the reduction of the tensile elongation in the Si(V) alloy was smaller than

Fig. 11 (a) Yield strength $\sigma_{0.2}$ and (b) tensile elongation ε_f of the base, Si(Ni), Si(Al) and Si(V) alloys.

those of the other alloys, maybe reflecting the degenerated eutectoid microstructure in the channel region.

4. Discussion

The solubility limit of Si in the present dual two-phase microstructure with a composition of Ni₇₅Al₉V₁₃Nb₃ was small irrespective of the substitution manner of Si for Ni, Al or V. From the engineering point of view, the present base alloy composition was enforced to contain Nb by which prominent solid solution strengthening was expected. However, it is known that Si prefers to combine with Nb.²⁰⁾ Consequently, the solubility limit of Si in the present alloy composition has to be reduced by the formation of the Ni₁₆Si₇Nb₆ (G phase) dispersions. In fact, any third-phase dispersions were not identified in the base alloy composition which Nb was removed from and 2 at% Si was added to.²¹⁾

In the XRD profiles shown in Fig. 7, the {220} reflection peaks were well separated for the base, 1Si(Ni) and 1Si(Al) alloys but not for the 1Si(V) alloy. This result indicates that the microstructure in the channel region depends on the substitution manner of Si for Ni, Al or V. The XRD profile of the 1Si(V) alloy reveals that the phase separation did not fully proceed in the channel region. In other words, the prior Al phase was not completely decomposed into the two intermetallic phases, revealing that the eutectoid microstructure in

the channel region is destabilized. According to the previous study on Ni-Al-V-X phase diagram where X is an alloying element, Si is an element destabilizing the two intermetallic phases (L1₂ and D0₂₂) and stabilizing the Al phase, and actually has been reported to have the effect of reducing the eutectoid temperature.¹⁶⁾ Consequently, the phase decomposition into the two intermetallic phases from the prior Al phase is more or less hindered in the alloys to which Si was added. In the 1Si(V) alloy, V content constituting the Ni₃V phase is more removed from the base alloy composition than in the other alloys. Therefore, it is likely that the decomposition into the two intermetallic phases was more hindered in the channel region of the 1Si(V) alloy. Similar substitution dependence of Si on the microstructure of the channel region has been observed in dual two-phase Ni₃Al and Ni₃V intermetallic alloys to which Re,²²⁾ Mo²³⁾ and W²³⁾ were added. These elements including Si were suggested to destabilize two intermetallic phases and stabilize Al phase.¹⁶⁾

For the hardness and yield strength of the alloys in which Si was soluble below the solubility limit, the 1Si(Al) and 1Si(Ni) alloys displayed hardening while the 1Si(V) alloy contrarily displayed softening. The behavior of the latter alloy is attributed to insufficient decomposition from the Al phase into the two intermetallic phases in the channel region, in other words, due to immature eutectoid microstructure in the channel region, as described earlier. In the dual two-phase intermetallic microstructures, it has been reported that the channel region consisting of eutectoid microstructure serves as hard material while the primary Ni₃Al precipitates serve as soft material,²⁴⁾ in contrast to the γ/γ' -type conventional superalloys. Consequently, the immature eutectoid microstructure in channel region of the 1Si(V) alloy had to result in the softening.

The 1Si(Al) alloy more hardened (strengthened) than the 1Si(Ni) alloy, as shown in the hardness behavior (Fig. 10) as well as the yield strength behavior (Fig. 11). Such a hardening (strengthening) behavior may be explained by solid solution hardening mechanism operating when adding Si is substituted for the constituent elements, Ni, Al and/or V. To experimentally evaluate solid solution hardening operating in the two constituent intermetallic phases of the two alloys, unit cell volume increment rates defined by $|dV/dC|$ were calculated, using the lattice parameters shown in Fig. 8 and plotted in Fig. 12. Here, V is a unit cell volume defined by $(a \times a \times a)$ in the case of the Ni₃Al phase and $(a \times a \times c/2)$ in the case of the Ni₃V phase, and C is concentration of Si (defined by at%). To equivalently evaluate the solid solution hardening in cubic structure and tetragonal structure, dV/dC instead of da/dC or dc/dC that is applicable to alloys with cubic structure was used. It is evident from the figure that the 1Si(Al) alloy showed larger $|dV/dC|$ value in the both phases than the 1Si(Ni) alloy. This result means that the lattice strain caused by the addition of Si to the alloy is larger in the 1Si(Al) alloy than in the 1Si(Ni) alloy, consequently resulting in larger solid solution hardening in the 1Si(Al) alloy than in the 1Si(Ni) alloy. Here, we again have to keep it in mind that the Si contents used in the calculation are nominal (overall) composition in the alloy but not the Si contents actually partitioned in the two constituent phases in the alloy. Also, relative contribution of the solid solution hardening due to Si in the Ni₃Al

Fig. 12 Unit cell volume increment rates defined by $|dV/dC|$ for the 1Si(Ni) and 1Si(Al) alloys, where V (nm^3) is unit cell volume and C (at%) is concentration of Si.

phase to that due to Si in the Ni_3V phase cannot be estimated because the partition of Si into the two intermetallic phases, the volume fraction of the two intermetallic phases and so on have not been measured in these alloys. This issue will be addressed in a coming paper.

5. Conclusion

The effects of Si addition on the microstructures and mechanical properties of dual two-phase Ni_3Al and Ni_3V intermetallic alloys with a composition of $\text{Ni}_{75}\text{Al}_9\text{V}_{13}\text{Nb}_3$ (formulated by at%) were investigated by SEM, EPMA, XRD, Vickers hardness and tensile test at room temperature, focusing on the substitution manner of Si for Ni, Al or V. The following results were obtained from the present study.

- (1) Solubility limit of Si in the present dual two-phase microstructure was less than 2 at% Si irrespective of the substitution manner of Si for Ni, Al or V. The eutectoid microstructure in the channel region was degenerated in the alloy in which Si was substituted for V.
- (2) Third-phase dispersions, $\text{Ni}_{16}\text{Si}_7\text{Nb}_6$ (G phase: D8a) were identified at grain boundaries of the alloys exceeding their solubility limits.
- (3) In the alloy in which Si was substituted for Ni, unit cell volume of the constituent Ni_3Al phase increased while that of the constituent Ni_3V phase little changed. In the alloy in which Si was substituted for Al, unit cell volumes of both phases decreased. Structural tetragonality of the constituent Ni_3V phase increased, irrespective of the substitution manner of Si.
- (4) The alloy in which Si was substituted for Al or Ni hardened (or strengthened) whereas the alloy in which Si was substituted for V softened.
- (5) The hardening in the alloys in which Si was substituted for Al or Ni was primarily attributed to solid solution

hardening due to Si substituted for the solvent atoms Ni, Al and/or V while the softening in the alloy which Si was substituted for V was attributed to degenerated eutectoid microstructure in the channel region.

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