MICROSTRUCTURE CONTROL OF Ni BASE ALLOYS WITH HIGH VOLUME FRACTION OF D₀₂₂ COMPOUND

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Abstract

Formation and morphology of A1/D₀₂₂ two-phase microstructure have been investigated in Ni-V alloys in order to study the fundamentals for microstructure control of wrought alloys containing high volume fraction of tetragonal compound. In the hypo-stoichiometric composition of Ni₃V, formation of "multi-variant structure (MVS)" consisting of D₀₂₂ single phase takes place below T₀ temperature. By aging in the A1/D₀₂₂ two-phase region, A1 phase is introduced into MVS via two different modes: precipitation with incoherent interfaces and continuous phase separation with coherent interfaces. The latter case is attractive because the interface between the two phases remains coherency after long-term aging at elevated temperatures, even though coarsening of D₀₂₂ phase occurs. In the binary alloy, the morphology of coherent two-phase microstructure becomes "maze", where the D₀₂₂ phase has plate in shape with irrational habit planes close to {304}_{D022}. The habit plane is parallel to one of the *a*-axes of D₀₂₂ and an invariant line between the two phases, since the misfit strains along *a*- and *c*-axes of D₀₂₂, δ_a and δ_c , respectively, have the relationship of $\delta_a < 0 < \delta_c$. The calculation based on the lattice invariant theory as well as experimental results clearly demonstrate that the misfit strain ratio δ_c/δ_a is a dominant factor to determine the habit plane and that the value of $|\delta_a|$ is the key factor for the shape of D₀₂₂ phase. The reduction in $|\delta_a|$ can change the shape drastically from plate into prism elongated along an *a*-axis, leading to the formation of thermally stable "chessboard" microstructure in the two-phase alloys.

Introduction

The volume fraction of Ni₃(Al, Ti)- γ' (L1₂) phase is one of the most important factors for high temperature strength in Ni base superalloys. The single-crystal superalloys usually contain more than 70 vol. % of γ' phase by means of composition control and heat treatment. On the other hand, wrought Ni base alloys usually have the volume fraction less than 50 %, because wide window is required for the hot working process. In the case of Waspaloy, the volume fraction is known to be limited up to 50 % at the most. However, the limitation can be overcome by using Kurnakov type compounds as strengtheners. This type of compounds has a congruent disordering temperature T_C, above which the wide range of process window exists. In addition, control of microstructure as well as the volume fraction (up to 100 %) can be possible through cooling process. Therefore, obtaining the fundamental knowledge for microstructure control using Kurnakov type compounds opens new possibility for developing new wrought Ni base alloys, especially for steam turbines of USC (ultra-super critical) power plants operated at over 700°C. In this study, we select Ni₃V as a model case based on the following two

reasons; one is the high T_C (1318 K) at its stoichiometric composition [1, 2], and the other is crystal structure of tetragonal D₀₂₂. This structure has two misfit strains against fcc (A1) matrix along *a*- and *c*-axes, while γ' phase has only one. It is known that Ni₃V coherently precipitates in Ni- γ matrix due to small lattice misfit strains [3], but no attempt has been made to control the morphology by misfit strains.

Recently, we examined the microstructure of Ni-25at%V quenched from high temperature A1 region [4, 5]. The high temperature A1 phase completely transforms to D₀₂₂ phase during quench (*V_f*=100%), and exhibits a fine coherent brick-like "multi-variant structure (MVS)" consisting of three variants of D₀₂₂ with *c*-axes perpendicular to each other. In the MVS, one of the three variants with quadrangular prism shape (major variant) of 90×90×150 nm has coherent interfaces of (101)_{D022}, ($\bar{1}01$)_{D022} and (010)_{D022}, in fcc base index. The major variant particles are periodically arrayed with an interval of 30 nm, and the remaining two channels parallel to {101}_{D022} and {010}_{D022} are filled with two other variants (minor variants) with their *c*-axes parallel to the *a*-axis of the major variant. The formation of MVS would be attributed to the minimization of the anisotropic strain fields due to the tetragonality against A1 matrix with the following lattice parameter relationship: $a_{D022} < a_{A1} < c_{D022}/2$ [2, 3]. Since the morphology of MVS is just like γ/γ' two-phase morphology in superalloys, if rotated 45° around [010] axis, it is attractive as high temperature material. However, this MVS is not stable at elevated temperatures, and drastically coarsens by coherency loss at interfaces [5, 6]. The collapse of MVS is caused by a release from elastic constraint, accompanied by the increase in the lattice parameter ratio *c/a* from nearly cubic value (2.006) to equilibrium value (2.04). Therefore, some modification to accommodate the elastic constraint is required to improve the thermal stability of MVS.

In this study, introduction of A1 phase into MVS has been attempted. First, we have focused on the hypo-stoichiometric composition of Ni₃V in the binary system, and identified the region to form MVS with A1 phase. Then, morphology control of the two-phase microstructure has been examined in terms of misfit strains through alloying.

Experimental Procedures

Four binary alloys with compositions of Ni-23V, Ni-20V, Ni-18V and Ni-17V (all compositions are given in atomic percent unless otherwise stated) were prepared in order to investigate the A1/D₀₂₂ two-phase microstructure. Ternary alloys containing Co, Nb or Fe were also prepared so as to change the misfit strains between A1 and D₀₂₂ phases against Ni-20V. Note that Co and Fe preferentially substitute Ni-sublattice while Nb substitutes V-sublattice in Ni₃V [7]. The five alloys of Ni-20V-10Co, Ni-15V-

5Nb, Ni-19.5V-2Fe, Ni-19V-4Fe and Ni-19V-6Fe, having 50–60 vol.% of D0₂₂ phase at 1073 K, were selected based on the reported binary and ternary diagrams [1, 2, 8–13]. All of these alloys were prepared by arc melting in argon atmosphere with a non-consumable tungsten electrode as 35 g button ingots, using 3N7 nickel pellets, 3N vanadium tablets, 3N cobalt lumps, 3N niobium grains and electrolytic iron. Each button ingot was melted five times by turning over each time in order to avoid segregation. These ingots were cut to pieces with a size of 6.0×6.0×10.0 mm³ by an electro-discharged machine.

All samples were homogenized at 1573 or 1523 K (A1 single phase region) for 3.6 ~ 10.8 ks, followed by water quench. These treatments were conducted using a specially designed vertical furnace under argon atmosphere [14]. Aging treatments were employed in the A1+D0₂₂ two-phase region: 1273 K for Ni-23V and 1073 K for binary Ni-(17–20)V and ternary alloys. All samples for aging were sealed off in silica capsules under argon back-filled after evacuating to 8×10⁻⁴ Pa. After holding the capsules for 0.9–8640 ks in the furnace, the samples were quenched into water quickly by breaking the capsules.

Microstructures were examined by transmission electron microscope (TEM). TEM discs with 0.15 mm in thickness and 3 mm in diameter were machined, then mechanically polished, followed by twin-jet electropolishing in a solution of ethanol with 12 vol. % perchloric acid at 253 K. The TEM observation was performed with an incident beam direction $\mathbf{B}=\langle 100 \rangle$ so as to distinguish the three variants of D0₂₂. The planes and directions of D0₂₂ phase are indexed in the same way as A1 structure, although the unit cell of D0₂₂ structure is twice of that of A1 along its *c*-axis. The misfit strains between A1 and D0₂₂ phases were calculated using selected area diffraction patterns obtained by means of microbeam method. The detail procedures will be described later.

Results and Discussion

Formation of A1/D0₂₂ Two-phase Microstructure

Before investigating the morphology of two-phase microstructure, it is important to identify the region to form MVS in hypo-stoichiometric alloys. Figure 1 shows TEM dark field images (DFIs) of the binary alloys with D0₂₂ phase. The typical MVS in quenched Ni-25V from 1573 K exhibits the major variant particles with square shape along $\langle 101 \rangle_{D0_{22}}$ and the size of 90 nm [Fig. 1(a)] surrounded by channels of minor variants [Fig. 1(b)] with coherent interfaces. These images were taken with $\mathbf{B}=010$, and only two variants of D0₂₂ are visible, as schematically shown in Fig. 1(f). Similarly, the quenched Ni-23V completely transforms to D0₂₂ phase and exhibits MVS as seen in Fig. 1(c) where only major variant is excited. The major variant with a particle size of about 50 nm (indicated by a white dotted square) covers all over the sample with narrow channels of minor variants. In case of Ni-20V, MVS is obtained after short time aging at 1073 K /0.9 ks, not in the quenched state where very fine D0₂₂ particles with 10 nm in size are distributed in A1 matrix. As shown in Fig. 1(d), the size of major variant particles in the MVS is about 20 nm. Note that this sample is not completely D0₂₂ single phase and some channels are filled with disordered A1 phase, but the morphology is quite similar to MVS. In Ni-18V, no D0₂₂ can be recognized in the quenched state. After aging at 1073 K /3.6 ks, it precipitates in A1 matrix as shown in Fig. 1(e), but the microstructure never becomes MVS even after further aging. In Ni-17V, only a small amount of D0₂₂ phase is recognized after

long-term aging. Thus, MVS is formed in the hypo-stoichiometric binary alloys [Fig. 1(c, d)], but the formation becomes more difficult as V content decreases below 19 at%.

The hypo-stoichiometric alloys showing MVS were further investigated. Figure 2 shows TEM images of Ni-23V and Ni-20V aged in A1/D0₂₂ two-phase region. After aging at 1273 K for 86.4 ks, Ni-23V exhibits coarse A1 phase with plate and particle shapes with the size of 100 ~ 500 nm in D0₂₂ matrix [Fig. 2(a)], and many dislocations are observed at the interfaces. On the other hand, Ni-20V aged at 1073 K /864 ks exhibits periodically aligned two-phase microstructure [Fig. 2(b)], where the bright and dark regions correspond to D0₂₂ and A1 phases, respectively. The shape of D0₂₂ phase is plate with about 130 nm in thickness, and A1 phase also has plate shape with about 70 nm in thickness. No dislocation is observed at the interfaces. In both cases, the selected area diffraction pattern (SADP) reveals the existence of only one variant of D0₂₂ phase, indicating that the major variant particles in MVS grow at the expense of minor variants and disordered A1 phase forms during aging. However, the formation mode of A1 phase is completely different; in Ni-23V, A1 phase precipitates incoherently at variant interfaces, whereas it forms coherently in Ni-20V. Figure 3 shows the change in volume fraction of D0₂₂ phase during the aging for the two alloys, together with those of other binary alloys. In Ni-23V, the volume fraction gradually decreases from 100 to 65 % with aging. In contrast, the quenched Ni-20V with a certain amount of A1 phase change to near single phase of D0₂₂ after short time aging (0.9 ks), and then the fraction starts decreasing to 65 % with aging. The interfaces in the two-phase microstructure keep coherency even after prolonged aging, indicating that the A1 phase should be formed spinodally through continuous composition change. Unlike these two alloys, the volume fraction increases with aging in the alloys with V content less than 18 at%.

From above results, there are three formation modes of A1/D0₂₂ two-phase microstructure, depending on the alloy composition and heat treatment temperature:

- 1) D0₂₂→D0₂₂+A1 (precipitation of A1, Ni-23V)
- 2) D0₂₂→D0₂₂+A1 (phase separation, Ni-20V)
- 3) A1→D0₂₂+A1 (precipitation of D0₂₂, Ni-(17–18)V)

The difference in the mode can be interpreted by the thermodynamic approach proposed by Soffa and Laughlin [15]. Figure 4 (a) shows a part of Ni-V binary diagram, showing the region where each mode occurs, together with the schematic Gibbs energy – composition curves of A1 (*G*_{A1}) and D0₂₂ (*G*_{D022}) phases at 1073 K [Fig. 4(b)]. Note that the phase boundaries of A1/A1+D0₂₂ and A1+D0₂₂/D0₂₂ are coherent boundaries drawn based on the measured volume fraction, with an assumption that molar volume of A1 and D0₂₂ phases are nearly equal, and they are consistent with other reports [8, 9].

The region to form MVS in hypo-stoichiometric compositions can be specified below *T*₀ temperature, as shown by hatching in Fig. 4(a). In this region, A1 phase becomes energetically unstable against D0₂₂ phase since *T*₀ is a trace of composition where the Gibbs energy of A1 and D0₂₂ at given temperatures are equal. In quenching, the higher the *T*₀, the easier the formation of MVS consisting of D0₂₂ phase, because the driving force for the A1→D0₂₂ phase transformation becomes large enough. This is the case for the quenched Ni-23V. With decreasing V content, however, the formation of MVS becomes more difficult because of lower supersaturation of V as well as slow diffusion rate even though the driving force is still enough to form MVS. This is the case for the quenched Ni-20V. Thus, once the sample is heated again at temperatures just below *T*₀, the ceased transformation

could proceed again, resulting in MVS.

The different formation modes of the two-phase mixture (1) and (2) by aging can be explained by introducing the miscibility gap in $D0_{22}$ phase. Then, the region showing MVS in the two-phase region in Fig. 4(a) can be divided further into two regions **A** and **B** sectioned by T_S line, where T_S is an inflection point ($\times$) on the $G_{D0_{22}}$ curve ($d^2G/dx^2=0$) in Fig. 4(b). The region **A** is inside the T_S point as well as the T_0 point, where the $G_{D0_{22}}$ curve has a positive curvature ($d^2G/dx^2>0$), so that the $D0_{22}$ phase is

energetically metastable against two-phase mixture as shown by the common tangent. This leads to a nucleation and growth of disordered A1 phase with a fixed composition marked by open circle on G_{A1} curve to reduce the chemical energy in the initial MVS state. The region **B**, on the other hand, is inside the T_0 point but outside of the T_S point, where the $G_{D0_{22}}$ has a negative curvature ($d^2G/dx^2<0$), so that the thermodynamically unstable $D0_{22}$ phase continuously decomposes to V-lean and V-rich ordered phases first, followed by phase separation to the stable A1

Figure 1. TEM DFIs of Ni-V binary alloys with $D0_{22}$ phase taken with $g=002_{D0_{22}}$ ($B=010_{A1}$): (a, b) typical MVS in the quenched Ni-25V from 1573 K showing (a) major and (b) minor variants, (c) MVS in the quenched Ni-23V from 1573 K showing major variant, (d) MVS in Ni-20V obtained after aging at 1073 K / 0.9 ks showing major variant, (e) $D0_{22}$ particles precipitated in Ni-18V aged at 1073 K / 3.6 ks. (f) Schematic illustration of MVS, together with $D0_{22}$ structure.

Figure 2. TEM images of the hypo-stoichiometric alloys showing different modes of two-phase microstructure formation ($B=100_{A1}$): (a) BFI of Ni-23V aged at 1273 K / 86.4 ks, (b) DFI of Ni-20V aged at 1073 K / 86.4 ks, $g=002_{D022}$.

Figure 3. Change in volume fraction of $D0_{22}$ phase in Ni-V binary alloys with aging in A1/ $D0_{22}$ two-phase region.

Figure 4. (a) Ni-V binary phase diagram showing the regions where different modes of two-phase microstructure formation take place. The thick lines are coherent phase boundaries. The hatched region is where MVS is formed. In the regions **A** and **B**, precipitation of A1 within $D0_{22}$ and continuous phase separation of $D0_{22}$ take place, respectively. (b) The schematic Gibbs energy – composition curves for A1 (G_{A1}) and $D0_{22}$ (G_{D022}) phases at 1073 K.

and $D0_{22}$ phases. The former is the case for Ni-23V aged at 1273 K whereas the latter is for Ni-20V aged at 1073K. The existence or absence of interfacial dislocations (Fig. 2) is one of the strong evidence to support these formation modes of A1 phase in $D0_{22}$ matrix. The other mode (3) in Ni-18V and Ni-17V is, just like opposite case of mode (1), where the alloy compositions are initially outside of the T_0 point on the positive curvature of G_{A1} , and the disordered single phase state is energetically unstable with respect to the stable two-phase mixture, resulting in precipitation of $D0_{22}$ phase in A1 matrix.

Morphology of Coherent A1/ $D0_{22}$ Two-phase Microstructure

The two-phase mixture in the region **B** is attractive because of the high volume fraction of $D0_{22}$ phase as well as the coherency of the interface even after long-term aging at elevated temperatures. However, the initial MVS is somehow coarsened, so that further improvement of thermal stability as well as morphology control of the two-phase microstructure are key issues for alloy development. In this section, we focus on the microstructure evolution of Ni-20V formed in the region **B** and identify the fundamental factors governing the microstructure morphology in terms of the misfit

strains between the two phases.

In the microstructure of Ni-20V [Fig. 2(b)], the diagonal plates of $D0_{22}$ phase are parallel to the edge-on planes close to $\{304\}_{D0_{22}}$. Another plates along $\langle 100 \rangle_{D0_{22}}$ were also confirmed to be parallel to $\{304\}_{D0_{22}}$ which are not edge-on [5]. Since there are four crystallographically equivalent $\{304\}_{D0_{22}}$ in the unit cell of $D0_{22}$, the morphology of this microstructure can be hereafter called as "maze".

The change in morphology from the initial MVS to maze microstructure is characterized by the following two points; (1) the change in shape of $D0_{22}$ from a quadrangular-prism into a plate by merging into each other, (2) the inclination of the habit plane from $\{101\}_{D0_{22}}$ to $\{304\}_{D0_{22}}$. Figure 5 shows change in the $A1/D0_{22}$ habit plane with aging. The habit plane is quantified as an angle θ between the edge-on habit plane and $(001)_{D0_{22}}$. The angle is 45° in MVS, and it gradually decreases to 35° . (1) and (2) take place simultaneously, but they are discussed separately in the following sections.

The $A1/D0_{22}$ Habit Plane. In order to identify the relationship between the habit plane and misfit strains, the lattice invariant theory [16] was applied to this study. Since the misfit strains between $A1$ and $D0_{22}$ phases are negative along a -axis (δ_a) and positive along c -axis (δ_c) in this system, formation of the irrational habit plane would be caused by the existence of an invariant line between the two phases. Figure 6(a) shows the schematic projection of lattices of $A1$ and $D0_{22}$ phases two-dimensionally depicted as a circle and an ellipse, respectively, on the coordinate of $[100]_{D0_{22}}$ and $[001]_{D0_{22}}$. The line connecting two intersection points is the invariant line. Based on the fact that all of the observed habit planes are parallel to one of the a -axes, the plane

Figure 5. Change in the $A1/D0_{22}$ habit plane angle of Ni-20V with aging at 1073 K. The habit plane is quantified as an angle θ between the edge-on habit plane and $(001)_{D0_{22}}$.

consisting of an invariant line and an a -axis would be the habit. Therefore, two-dimensional treatment can be applied. The habit plane angle θ corresponds to the angle between the invariant line and $[100]_{D0_{22}}$ (a -axis). Thus, the $\theta (= \tan^{-1}(y/x))$ can be geometrically calculated using the following circle and ellipse equations;

$$x^2 + y^2 = 1 \quad (A1 \text{ lattice})$$

$$\frac{x^2}{(1+\delta_a)^2} + \frac{y^2}{(1+\delta_c)^2} = 1 \quad (D0_{22} \text{ lattice})$$

where x and y are the coordinate of the intersection point. Then, the θ can be simply expressed as functions of the misfit strains;

$$\theta = \tan^{-1} \sqrt{\frac{-(1+2\delta_a^{-1})(\frac{\delta_c}{\delta_a} + \delta_a^{-1})^2}{\frac{\delta_c}{\delta_a}(\frac{\delta_c}{\delta_a} + 2\delta_a^{-1})(1+\delta_a^{-1})^2}}$$

This equation indicates that θ depends on both the misfit strain of δ_a and the ratio of misfit strains δ_c/δ_a . Figure 6(b) shows a plot of calculated θ as a function of misfit strain ratio using the above equation at two fixed values of δ_a : one (thick line) is the case of $\delta_a = -0.003$, and the other (thin line) is $\delta_a = -0.030$. In both cases, the angle θ apparently approaches to 45° as the misfit ratio approaches to -1 , and the deviation of θ between the two calculated lines is as much as 2° , even though the δ_a is changed by an order of magnitude. This result indicates that the habit plane strongly depends on the misfit strain ratio.

In order to verify the prediction, the misfit strains are measured in the sample of Ni-20V aged at 1073 K / 864 ks. Since all fundamental reflections of $D0_{22}$ structure coincide with those of $A1$ structure, it is impossible to measure misfit strains between these phases using conventional diffraction patterns. Then, microbeam method was applied in this study. The diameter of microbeam is small enough (10~40 nm) to obtain a diffraction pattern from each phase region. Figure 7 shows TEM DFI [Fig. 7(a)] and the microbeam diffraction patterns of $A1$ [Fig. 7(b)] and $D0_{22}$ [Fig. 7(c)] phases taken from the neighboring regions indicated by white circles in Fig. 7(a). Since the lattice parameters are inversely proportional to the distance of two reflections, δ_a and δ_c can be expressed as follows, using r_{A1} , r_a and r_c , which are indicated in Fig. 7(b, c):

$$\delta_a = \frac{a_{D0_{22}} - a_{A1}}{a_{A1}} = (r_{A1}/r_a) - 1$$

$$\delta_c = \frac{c_{D0_{22}}/2 - a_{A1}}{a_{A1}} = (r_{A1}/r_c) - 1$$

The obtained misfit strains are shown in Table I, together with the observed and calculated angles of habit plane. The values of δ_a and δ_c are about -0.003 and $+0.006$, respectively, and the misfit strain ratio is about -2 . Then, θ is calculated as 34.5° . This value agrees well with the observed value of 36.5° . Thus, the inclination of habit plane with aging is associated with the continuous change in misfit strains due to the phase separation.

The Shape of $D0_{22}$ Phase. The change in the shape of $D0_{22}$ phase during aging is related to the growth directions of initial particle. The growth along two directions, an a -axis and the invariant line,

Figure 6. Relationship between the A1/D0₂₂ habit plane and misfit strains: (a) the schematic projection of lattices of A1 and D0₂₂ phases depicted as a circle and an ellipse on the coordinate of [100] and [001], showing the existence of an invariant line in case of $\delta_a < 0 < \delta_c$, (b) calculated angle of invariant line as a function of misfit strain ratio δ_c/δ_a with fixed δ_a of -0.003 (thick line) and -0.030 (thin line).

is necessary to form plate shape observed in Ni-20V. In other words, the plate shape is the case that the growth rate along a -axis (v_a) and the invariant line (v_i) are on the same level. Based on the fact that the direction with smaller misfit becomes preferred direction to grow, as is clear in case of Ni₃Nb- δ phase [17], v_a depends on the value of $|\delta_a|$. Thus, the value of $|\delta_a|$ should be the key factor for the shape of D0₂₂. Based on this prediction, reduction in $|\delta_a|$ would be effective in improving the coarsened morphology of D0₂₂ by suppressing the growth along the invariant line, since v_a becomes larger than v_i ($v_a > v_i$).

Microstructure Control of A1/D0₂₂ Two-phase Alloys

In the previous section, δ_c/δ_a and $|\delta_a|$ are found to be the key factors for the habit plane and the shape of D0₂₂, respectively.

Figure 7. Measurement of misfit strains, δ_a and δ_c , using microbeam diffraction method: (a) TEM DFI and SADP of Ni-20V aged at 1073 K /864 ks ($B=100$), (b, c) microbeam diffraction patterns of A1 and D0₂₂ obtained from the regions marked with white circles in (a).

Table I. Measured misfit strains between A1 and D0₂₂ phases in Ni-20V aged at 1073 K /864 ks, together with observed and calculated angles of habit plane

Lattice misfit strain		θ / degree (observed)	θ / degree (calculated)
δ_a	δ_c		
-0.0027	0.0058	36.5	34.5

Based on the findings, an attempt has been made to control the two-phase microstructure by changing the misfit strains through alloying.

Table II shows effect of third element addition to Ni-25V on the lattice parameters of A1 and D0₂₂ phases in alloys which become single phase of A1 and D0₂₂ at 1473 K and 1273 K, respectively [7]. From these lattice parameters, misfit strains between the two phases can be calculated. In the stoichiometric Ni-25V, δ_a and δ_c are -0.0054 and +0.0130, respectively. Additions of Co (Ni site) and Nb (V site) decrease $|\delta_a|$, and the effect of Nb is more obvious than that of Co. However, δ_c decreases by Co addition, whereas it increases by Nb addition. On the other hand, addition of Fe to Ni site increases $|\delta_a|$, while δ_c remains almost unchanged. Although these misfit strains cannot be directly applied to the microstructure consisting of two phases with different

compositions, these trends can be referred for predicting the effects of the third element on the A1/D0₂₂ two-phase microstructure. In the early stage of continuous phase separation (D0₂₂→D0₂₂+A1), these trends would be helpful, since the compositions of the two phases are very close to each other. However, after prolonged aging, partition coefficients of Ni and M between the two phases have to be taken into consideration, since the lattice parameters also depend on Ni content [2, 3]. According to Table II, it is expected that addition of Co and Nb are effective in suppressing the coarsening of D0₂₂ along the invariant line. On the other hand, Fe addition is expected to maintain the shape unchanged. Figure 8 shows TEM images of two-phase microstructure in ternary alloys aged at 1073 K for 864 ks. In the alloy with 10%

Co [Fig. 8(a)], the microstructure observed from **B**=010_{A1} consists of two variants of D0₂₂ (dark) with parallelogram shape and A1 phase (bright) with rhombic shape aligned alternately, exhibiting so-called "chessboard" microstructure. Since all of the observed habit planes in this figure are edge-on, the morphology of both phases are prism shape elongated along *a*-axis. The habit plane is close to {304}_{D022}. In case of 5% Nb addition, however, "chessboard-like" microstructure is obtained as shown in Fig. 8(b). The morphology of D0₂₂ phase is recognized to be prism elongated along *a*-axis, but unlike the Co added alloy, the cross sectional shape is somehow irregular parallelogram and the habit plane is much closer to (001)_{D022}. In contrast, Fe added alloys remain the "maze" microstructure [Fig. 8(c)], regardless of Fe content [5].

Table II. Effect of third element M (M: Co, Nb, Fe) addition to Ni-25V on the lattice parameters of A1 and D0₂₂ phases and misfit strains between the two phases with the same composition

Alloy composition / at%	Lattice Parameter / Å			Misfit strain	
	A1 ¹⁾	D0 ₂₂ ²⁾			
	<i>a</i>	<i>a</i>	<i>c</i> / 2	δ _{<i>a</i>}	δ _{<i>c</i>}
Ni-25V	3.562	3.543	3.608	-0.0054	0.0130
Ni-25V-7Co	3.564	3.549	3.604	-0.0042	0.0111
Ni-23V-2Nb	3.567	3.554	3.618	-0.0038	0.0141
Ni-25V-3Fe	3.564	3.544	3.611	-0.0058	0.0129

¹⁾ Water quenched from 1473 K, ²⁾ Water quenched from 1273 K

Figure 8. TEM images of A1/D0₂₂ two-phase microstructure in Ni-V-M (M: Co, Nb, Fe) ternary alloys aged at 1073 K for 864 ks taken with **B**=100_{A1}; (a) Ni-20V-10Co (BFI), (b) Ni-15V-5Nb (BFI) and (c) Ni-19V-4Fe (DFI).

Table III. Misfit strains measured by microbeam method in the binary and the ternary alloys with Co, Fe and Nb aged at 1073 K /864 ks, together with the morphology (habit plane angle and shape) of D0₂₂ phase

Alloy composition / at%	Lattice misfit strain			θ / degree (observed)	Shape of D0 ₂₂
	δ_a	δ_c	δ_c / δ_a		
Ni-20V	-0.0027	0.0058	-2.14	36.5	plate
Ni-20V-10Co	-0.0020	0.0039	-1.97	37.7	prism
Ni-15V-5Nb	-0.0015	0.0110	-7.36	—	prism
Ni-19.5V-2Fe	-0.0031	0.0069	-2.20	38.8	plate
Ni-19V-4Fe	-0.0060	0.0077	-1.29	40.5	
Ni-19V-6Fe	-0.0061	0.0067	-1.10	43.6	

Table III shows measured misfit strains, together with observed habit plane angle and the shape of D0₂₂. In all alloys, δ_a and δ_c are negative and positive, respectively, and $|\delta_c|$ is larger than $|\delta_a|$. By comparing the value of δ_a , it is clear that the shape of D0₂₂ phase is plate in alloys with $|\delta_a| \geq 0.0027$ (Ni-20V and Fe added alloys) and prism in alloys with $|\delta_a| \leq 0.0020$ (Co and Nb added alloys). This result agrees well with the prediction, and there is no dependency on δ_c , although δ_c is small in Co added alloy (+0.0039) while it is much larger in Nb added alloy (+0.011). Thus, the value of δ_a is a key factor for control of the morphology, and the threshold exists at around $|\delta_a| = 0.002$.

Figure 9 shows change in the habit plane angle [Fig. 9(a)] and misfit strain ratio [Fig. 9(b)] as a function of M content (M: Co, Fe). In Ni-20V, the value of θ is 36.5°. Addition of Co has little effect on the change in the habit plane and the angle θ is 37.7° even by 10% addition. On the other hand, the angle θ is sensitive to Fe content. It increases linearly toward 45°, which is {110}_{D022} habit plane, with increase in Fe content. In the mean time, misfit strain ratio increases from -2 to -1 by Fe addition, although it remains almost unchanged by Co addition. Thus, it is clear that the habit plane can be controlled by misfit ratio and becomes {101}_{D022} when the ratio becomes -1, as predicted in Fig. 6. This is also consistent with the result of Nb added alloy, which exhibits the habit planes much closer to (001)_{D022} and has large misfit strain ratio of -7.

All of these above results are the cases that the invariant line exists between the two phases due to $\delta_a < 0 < \delta_c$. Figure 10 shows whole picture of the morphology map of D0₂₂ phase as functions of δ_a and δ_c , together with the plots obtained in this study. In the region of $\delta_a < 0 < \delta_c$ and $|\delta_a| < |\delta_c|$, it is clear that the value of δ_a is a factor determining the microstructure morphology, either maze or chessboard microstructure, regardless of δ_c . On the other hand, in the region without invariant line, the relative relationship between the misfit strains, $\delta_a < \delta_c$ or $\delta_a > \delta_c$, is important, because the morphology of D0₂₂ phase becomes elongated along directions with minimum misfit strain. For example, the morphology of Ni₃Nb- γ " phase, which is a metastable D0₂₂ phase in wrought Ni-base superalloys such as Inconel 718, is disc shape with habit plane of (001)_{D022}, since δ_a and δ_c are +0.009 and +0.037, respectively [18]. In the case of $\delta_a > \delta_c > 0$, the morphology should become a rod shape elongated along c -axis. In addition, in the case of metastable (Cu, Ni)₃Sn phase, the misfit strains δ_a and δ_c were reported to be +0.038 and -0.003, respectively [19]. These values imply the existence of invariant line, but observed morphology is rod shape elongated along c -axis. This is reasonable because of $|\delta_a| \gg |\delta_c|$, so that the θ becomes close to 90°, leading to the preferred growth along the c -axis.

Figure 9. Change in the habit plane angle (a) and misfit strain ratio (b) with M content (M: Co, Fe) in ternary alloys aged at 1073 K /864 ks.

Finally, from the viewpoint of thermal stability of MVS, chessboard microstructure is the most attractive, since the coarsening of D0₂₂ phase takes place only along an a -axis. Thus, control of misfit strains to be $|\delta_a| < 0.002$ and $\delta_c/\delta_a \approx -1$ is effective in preventing drastic morphology change of D0₂₂ phase at elevated temperatures.

Conclusion

1) In the hypo-stoichiometric composition, MVS of D0₂₂ phase is formed below T_0 temperature. By aging in the A1/D0₂₂ two-phase

Figure 10. Morphology map of coherent $D0_{22}$ phase in Al matrix plotted as functions of misfit strains. The investigated alloys in this study ranges in the hatched region ($\delta_a < 0 < \delta_c$, $|\delta_a| < |\delta_c|$). $\delta_a = -0.002$ is the threshold value for microstructure morphology, maze or chessboard. In the region without invariant line, the $D0_{22}$ has a shape elongated along the direction with less misfit strain.

region, Al phase is introduced into MVS by two different modes; precipitation with incoherent interfaces (above T_S) and continuous phase separation (below T_S). The latter case is attractive because interface between the two phases remains coherency after long-term aging.

2) In the coherent Al/ $D0_{22}$ two-phase microstructure, the plane parallel to an a -axis of $D0_{22}$ and the invariant line between the two phases becomes the habit. The shape of $D0_{22}$ phase becomes either plate or prism, depending on the relative growth rate along an a -axis and the invariant line.

3) Control of the morphology of $D0_{22}$ phase is possible by changing misfit strains ($\delta_c < 0 < \delta_a$). The misfit strain ratio δ_c/δ_a is the dominant factor to determine the habit plane, and the habit plane becomes $\{101\}_{D0_{22}}$ when the ratio becomes close to -1. On the other hand, the value of $|\delta_a|$ can change the shape of $D0_{22}$ phase from plate to prism when $|\delta_a|$ becomes smaller than 0.002, leading to the change in the microstructure morphology from maze to chessboard.

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References

1. J.F. Smith, and O.N. Carlson, "The Ni-V (Nickel-Vanadium) System," *Bull Alloy Phase Diagrams*, 3 (1982), 342-348.
2. W.B. Pearson, and W.J. Hume-Rothery, "The Constitution and Structure of Nickel-Vanadium Alloys in the Region 0-60 At.-% Vanadium," *J Inst Metals*, 80 (1952), 641-652.
3. K-M. Chang, "On the Habit Plane of γ -Ni₃V Precipitates," *Acta Metall*, 30 (1982), 961-964.

4. A. Suzuki, M. Takeyama, and T. Matsuo, "A1→D0₂₂ transformation and multi-variant structure of Ni₃V," *Defect Properties and Related Phenomena in Intermetallic Alloys*, ed. E.P. George, H. Inui, M.J. Mills, and G. Eggeler, (Warrendale, PA: Materials Research Society, 2003), 753, 363-368.
5. A. Suzuki, "Microstructure Evolution and Morphology of D0₂₂ Compound in Ni Base Alloys," (Ph.D. thesis, Tokyo Institute of Technology, 2003).
6. A. Suzuki, H. Kojima, T. Matsuo, and M. Takeyama, "Alloying effect on stability of multi-variant structure of Ni₃V at elevated temperatures," *Intermetallics*, 12 (2004), to be published.
7. M. Okihashi, "Alloying effect on the crystal structure of Ni₃V-γ," (Master thesis, Tokyo Institute of Technology, 2002).
8. H.A. Moreen, R. Taggart, and D.H. Polonis, "The Formation of Modulated Structures in Ni-V Alloys," *Metall Trans*, 5 (1974), 79-90.
9. S. Kobayashi, T. Sumi, T. Koyama, and T. Miyazaki, "Determination of coherent phase boundaries in Ni-V and Ni-Mo alloys by utilizing macroscopic composition gradient," *J Japan Inst Metals*, 60 (1996), 22-28.
10. K.P. Gupta, S.K. Mukherjee, A.K. Jena, and S.B. Rajendraprasad, "The Cobalt-Nickel-Vanadium System," *J Alloy Phase Diagrams*, 3 (1987), 105-115.
11. R. Nino, T. Mohri, Y. Terada, C-S. Oh, and T. Suzuki, "Phase diagram of Ni₃V-Co₃V pseudobinary system," *J Phase Equilibria*, 20 (1999), 29-34.
12. G.V. Raynor, and V.G. Rivlin, "Phase Equilibria in Iron Ternary Alloys. X. –Critical Evaluation of Constitution of Cobalt-Iron-Vanadium System," *Int Met Rev*, 28 (1983), 211-227.
13. T. Ueyama, M.M. Ghanem, N. Miura, M. Takeyama, and T. Matsuo, "Phase stability of Ni₃Nb-δ phase in Ni-Nb-M systems at elevated temperatures," *THERMEC '97*, ed. T. Chandra and T. Sakai (Warrendale, PA: TMS/AIME, 1997), 1753-1760.
14. A. Suzuki, M. Takeyama, and T. Matsuo, "Transmission electron microscopy on the phase equilibria among β, α and α₂ phases in Ti-Al binary system," *Intermetallics*, 10 (2002), 915-924.
15. W.A. Soffa, and D.E. Laughlin, "Decomposition and Ordering Process Involving Thermodynamically First-Order Order → Disorder Transformations," *Acta Metall*, 11 (1989), 3019-3028.
16. U. Dahmen, "Orientation Relationship in Precipitation Systems," *Acta Metall*, 30 (1982), 63-73.
17. M. Takeyama, H. Yokota, M.M. Ghanem, and T. Matsuo, "Phase Equilibria and Microstructure Control Using Ni₃Nb-δ Phase in Ni-Nb-Fe Ternary System at Elevated Temperatures," Special Issue: *J Materials Processing Technology*, Ed. T. Chandra, K. Higashi, C. Suryanarayana, and C. Tome (Elsevier Science, UK, 2001), 117-3, Section D7 [CD-ROM].
18. J.M. Oblack, D.H. Paulonis, and D.S. Duvall, "Coherency Strengthening in Ni-Base Alloys Hardened by D0₂₂-γ" Precipitates," *Metall Trans*, 5 (1974), 143-153.
19. J-C. Zhao, and M.R. Notis, "Spinodal decomposition, ordering transformation, and discontinuous precipitation in a Cu-15Ni-85Sn alloy," *Acta Materialia*, 46 (1998), 4203-4218.