Effect of Rh and V Additions on Plastic Deformation Behaviour in Ni3Nb Single Crystals with D0a Structure

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The effect of Rh and V additions on phase stability and plastic deformation behaviour in Ni3Nb single crystals with the D0a structure was investigated, focusing on the slip behaviour of (010)[100], (010)[001] and (001)[100] systems in a wide temperature range between room temperature and 1200°C. The V addition induces no significant change in the critical resolved shear stress (CRSS) for (010)[100] slip at low temperatures, while the Rh addition is effective in increasing the CRSS at temperatures below 500°C and above 800°C, resulting in significant improvement of high-temperature strength. The increment of high-temperature strength is closely related to suppression of the climb motion of edge dislocations. The Rh addition also effectively increases the CRSS for (010)[001] and (001)[100] slip. The V addition was expected to enhance activation of the (010)[001] slip by reducing the SISF energy between the superpartials, but that was not achieved.

(Received March 20, 2002; Accepted July 17, 2002)

Keywords: intermetallic compounds; dislocations; high temperature mechanical properties; yield phenomena

1. Introduction

Many A3B-type intermetallic compounds with geometrically close-packed (GCP) structures are known to show superior mechanical properties and interesting plastic behaviour such as anomalous strengthening. The compounds are constructed by various stacking sequences with a combination of two-fold hexagonal layer (h-layer) and three-fold cubic layer (c-layer). In addition, some types of ordered arrangement are produced on the close-packed plane such as triangular (T-type), rectangular (R-type) and compound-type (TR-type). The plastic behaviour depends strongly on the phase stability of the related structure.

Ni3Nb with the D0a ordered structure, which is one of the A3B-type compounds has been of interest as a strengthening component in Ni-based superalloys. Recently, our group identified the deformation mode and examined the plastic behaviour of Ni3Nb single crystals; four slip systems of (010)[100], (010)[001], (001)[100] and (201)[102], and three twinning systems of (211)[010 7 13], (011)[011] and (012)[021] are operative and strongly dependent on crystal orientation and test temperature. The critical resolved shear stress (CRSS) for (010)[100], (001)[100] and (201)[102] slips exhibits anomalous increase as temperature rises.

Figure 1 shows the D0a structure for Ni3Nb and other related structures of D022 and D019. The D0a structure is classified as an orthorhombic system because B atoms are arranged in rectangular fashion on the close-packed (010) plane. However, since the atomic arrangement and stacking sequence of the (010) plane are identical to those on the (0001) basal plane in a simple hcp lattice, the D0a structure also can be identical to an hcp lattice based structure with an R-type close-packed layer.

The relation between the relative phase stability and plastic behaviour in the GCP phases has been extremely investigated particularly in compounds with the L12 structure. In addition, Suzuki pointed out the relation between phase stability and planar fault energy in A3B-type compounds. The concept can be applied for Ni3Nb as follows.

The D022 and D019 structures are closely related to the D0a structure; introduction of 1/3[001] and 1/2[100] shift vector on (010) and (001) in the D0a structure creates a local stacking of {112} layers of the D022 structure and (010) layers of the D019 structure in the D0a structure, respectively. Therefore, addition of an alloying element which stabilizes the D022 and D019 structures may decrease the energy of the superlattice intrinsic stacking fault (SISF) on (010) and the anti-phase boundary (APB) on (001), respectively. Thus, V and Rh addition may change the fault energy in Ni3Nb because Ni3V and Rh3Nb crystallise in the D022 and L12 structures, respectively. The D019 structure can be considered as an intermediate structure between the D0a and L12 from the viewpoint of phase stability, since the atomic configuration of the close-packed plane and stacking sequence changes from the D0a to L12 through D019. In our preliminary work, a large Rh addition to Ni3Nb was confirmed to transform the crystal structure from D0a into D019. Hence, addition of V and Rh is believed to decrease the SISF energy on (010) and the APB energy on (001) in Ni3Nb, respectively.

It should be noted that the phase stability of an A3B-type compound is closely related to its mechanical properties. Anomalous increase of yield stress is known to occur due to Kear-Wilsdorf (K-W) locking of \{110\} superlattice dislocations in Ni3Al with the L12 structure (for example, see references) and the magnitude of anomalous strengthening is enhanced by reducing the stability of the L12 structure with respect to other close-packed structures. Moreover, variation in fault energy often changes the core structure of a superlattice dislocation, which influences the plastic deformation behaviour.

This paper describes the effect of Rh and V addition on plastic deformation behaviour, especially by slip on (010)[100], (010)[001] and (001)[100] in Ni3Nb single crystals with the D0a structure.

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2. Experimental Procedure

Master ingots were prepared from high-purity Ni, Nb, V and Rh by arc-melting under high purity argon gas. The nominal compositions of binary and Rh-doped and V-doped ternary Ni$_3$Nb-based alloys were Ni$_3$Nb, (Ni$_{0.95}$Rh$_{0.05}$)$_3$Nb and Ni$_3$(Nb$_{0.97}$V$_{0.03}$), respectively. Single crystals were grown by the floating zone method using an NEC SC-35HD furnace at a rate of 2.5 mm h$^{-1}$ in a high purity Ar gas flow. Rectangular specimens for compression tests with dimensions of approximately $2 \times 2$ mm$^2 \times 5$ mm and plate specimens for tensile tests with the gauge dimensions of approximately $2 \times 1$ mm$^2 \times 5$ mm were prepared by electro-discharge machining from as-grown single crystals. $[110]^*$ and $[331]^*$ orientations were chosen for loading axes in compression tests and the $[205]^*$ orientation was selected in tensile tests. An asterisk (*) indicates the reciprocal-lattice representation. The detailed preparation method including the Schmid factors for each orientation can be found in our previous papers. 5, 8) Compression and tensile tests were performed on an Instron-type testing machine at a nominal strain rate of $1.7 \times 10^{-4}$ s$^{-1}$ in a vacuum. Compression tests were conducted in the range from room temperature (RT) to 1200$^\circ$C and tensile tests in the range from RT to 1000$^\circ$C. Operative deformation modes were determined by slip-trace analysis on two orthogonal surfaces of the specimens observed by an optical microscope with Nomarski interference contrast. Deformation substructure was observed in a Hitachi H-800 transmission electron microscope (TEM) operated at 200kV and a JEOL JEM 3010 operated at 300 kV.

3. Results

3.1 Plastic behaviour deforming by slip on (010)[$100$]

Single slip on (010)[$100$], which corresponds to (010)[$12\overline{1}$] basal slip in the hcp notation, was reported to be operative in binary Ni$_3$Nb single crystals in the $[110]^*$ orientation at all test temperatures. 5) The (010)[$100$] slip system was also confirmed to operate in both ternary crystals. Figure 2 shows the temperature dependence of the CRSS for (010)[$100$] slip in V-doped and Rh-doped ternary and binary Ni$_3$Nb single crystals deformed in the $[110]^*$ orientation in compression. In our previous study in binary Ni$_3$Nb, 5) (010)[$100$] slip showed anomalous strengthening behaviour due to the K-W locking process on the basis of the microscopic cross-slip of a 1/2[$100$] superpartial dislocation from the (010) slip plane to the (001) due to the difference in APB energies on (010) and (001), which is analogous to that in Ni$_3$Al. Anomalous increase of CRSS for slip on (010)[$100$] was also observed in ternary single crystals, but the CRSS-temperature behaviour was influenced by addition of the alloying elements.
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The trend of the overall CRSS-temperature relation in V-doped ternary Ni$_3$Nb is quite similar to that in the binary crystal. There is no significant difference in CRSS between binary and V-doped ternary crystals at low temperature, but the peak stress is decreased by V addition. Above the peak temperature, the rate of decrease in CRSS is moderated by V addition resulting in higher CRSS than that in binary crystals at high temperatures.

CRSS-temperature relation for Rh-doped ternary crystals show significant difference from that for binary crystals. The CRSS in Rh-doped ternary crystals is considerably higher than that in binary crystals deformed at low temperatures. The CRSS in Rh-doped ternary crystals increases anomalously as the deformation temperature rises, and the CRSS-temperature curve shows a broader peak than that in binary crystals at high temperatures.

To clarify the anomalous strengthening mechanism in binary and ternary Ni$_3$Nb crystals at high temperatures, the strain-rate dependence of flow stress was examined by strain-rate jump tests. Figure 3 shows variation in the stress-strain curves of Rh-doped Ni$_3$Nb single crystals with an abrupt change of strain rate at various temperatures. The strain rate sensitivity (SRS) of flow stress was negligible below 900°C, while the SRS gradually increased with temperatures above 900°C. At 1100°C, the stress amplitude due to abrupt change of strain rate reached 100 MPa.

Figure 4 shows the temperature dependence of the activation volume ($V^*$) determined from the SRS of the flow stress using eq. (1).

$$V^* = kT (\Delta \ln \dot{\varepsilon} / \Delta \tau)$$

where $k$, $T$, $\Delta \tau$ and $\dot{\varepsilon}$ are the Boltzmann constant, test temperature, change in the resolved shear stress with the abrupt change of strain rate and the strain rate, respectively. $\Delta \tau$ was determined from the difference between the steady state flow stress at around 1% plastic strain by abrupt change of the strain rate from $1.7 \times 10^{-4}$ s$^{-1}$ to $1.7 \times 10^{-3}$ s$^{-1}$. The activation volume of Rh-doped ternary crystals shows a very high value of about 800$b^3$ ($b$: the magnitude of Burgers vector of 1/2[100] superpartial dislocation) at 900°C, but it rapidly decreases with increasing temperature and exhibits a small value above 1100°C. The shape of the activation volume-temperature curve of Rh-doped ternary crystals is quite similar to that of binary crystals, but the curve of Rh-doped crystals shifts to a 100°C higher temperature than that of binary crystals.

Figure 5 shows the dislocation structure on the (010) slip plane in Rh-doped ternary crystals deformed along the [110]$^*$ axis at high temperatures where the rapid change in activation volume was observed. At 900°C, almost all [100] dislocations had a screw character and were straightly aligned. The morphology was quite similar to that at low temperatures. At 1100°C, however, dislocations with pure edge character existed in addition to the straight screw dislocations. At 1100°C, dislocations with screw character were hardly observed and most dislocations were straightly aligned with edge character. The variation in dislocation morphology with increasing tem-
perature showed good correlation with the change in the activation volume; as the density of edge dislocations increased, the activation volume decreased. This tendency was also confirmed for the binary Ni₃Nb. In the binary Ni₃Nb crystal, edge dislocations appeared in addition to screw dislocations at 900°C. Above 1000°C, most dislocations had an edge character with a wavy shape and a large number of dislocation loops were also observed. The temperature for transition of the dominant dislocation character from screw to edge rose from 900°C to 1000°C with Rh additions. This is in good agreement with the variation in activation volume with test temperature; the activation volume-temperature curve increased by 100°C with Rh addition. It is obvious that the variation in activation volume directly reflects the change in the dislocation structure. The broad peak of the CRSS-temperature curve for Rh-doped ternary crystals in Fig. 2 may be due to there being two different mechanisms for the motion of dislocations. The motion of screw dislocations controls the plastic deformation between 800°C and 1000°C, while that of edge dislocations dominates the flow stress between 1000°C and 1100°C. Both mechanisms therefore contribute to improve high-temperature strength. The detailed mechanism for the high-temperature strengthening in Rh-doped Ni₃Nb is discussed in Section 4.1.

3.2 Plastic behaviour deforming by slip on (010)[001]

The (010)[001] slip system is operative at temperatures above 800°C in binary Ni₃Nb crystals deformed along some compressive axes. Activation of (010)[001] slip is important to improve the deformability in polycrystalline Ni₃Nb from the viewpoint of the number of operative slip systems. In addition, (010)[001] slip is known to act as an important deformation mode to accommodate the stress concentration at the intersection of deformation twins.

A [001] superlattice dislocation can be dissociated into 1/3[001] and 2/3[001] superpartial dislocations bound by a SISF. A large number of dislocations bound by an SISF were actually observed in Ni₃Ta with the D₀₂₁ structure. The energy of the SISF created between the two superpartials may be closely related to the phase stability of the D₀₂₁ and D₀₂₂ structures as previously pointed out. When an SISF is introduced on (010) by dissociation of [001] dislocations in the D₀₂₁ structure, four [112] layers of the D₀₂₂ structure are locally created within that structure. Therefore, it is speculated that addition of an alloying element such as V which crystallises in the D₀₂₂ structure decreases the SISF energy in the D₀₂₁ structure, and this may be effective in enhancing the activity of slip on (010)[001] in this structure.

Figure 6 shows the temperature dependence of the CRSS in binary and ternary V-doped and Rh-doped Ni₃Nb single crystals deformed in the [331]* orientation. (010)[001] slip was observed at low and intermediate temperatures for binary and ternary crystals. The trend in the CRSS-temperature relation is the same as that observed in the [110]*-oriented crystals below the peak. However, the transition of slip systems from (010)[001] to (010)[001] occurred around the peak temperature for anomalous strengthening and the CRSS for
(010)[001] slip rapidly decreased above the peak temperature. Transition of the slip system was clearly confirmed by the change in contrast of the slip traces on the (320) and (116) specimen surfaces. The transition temperature of operative slip systems was determined to be around 800°C for binary and V-doped ternary crystals and around 900°C for Rh-doped ternary crystals, respectively. V addition induced no significant effect on the transition temperature, while Rh addition shifted the transition temperature higher by 100°C and increased the CRSS for (010)[001] slip.

Figure 7 shows weak beam dark-field images of [001] dislocations in binary and V-doped ternary Ni_3Nb crystals deformed in the [331]∗ orientation at 900°C. Most dislocations exhibit oscillatory contrast. Widely dissociated segments of dislocations with fringe contrast are seen at the parts indicated by small arrows. Most dislocations are narrowly dissociated into two superpartials approximately 9 nm in width in both crystals, suggesting little change of SISF energy by the V addition.

3.3 Plastic behaviour deforming by slip on (001)[100]

The (001)[100] slip system in Ni_3Nb corresponds to \{101\}⟨12\bar{1}0⟩ prism slip in the hcp notation. The [100] dislocation on the (001) plane was widely dissociated into two \{1\}/2[100] superpartials bound by an APB in binary Ni_3Nb.\(^9\)

The APB energy on the (001) plane in the D0\(_a\) structure is closely related to the phase stability with respect to the D0\(_{19}\) structure. Rh addition is believed to reduce the APB energy on (001) in Ni_3Nb and to affect the plastic deformation behaviour by slip on (001)[100].

The single slip on (001)[100] could not be realized in compression at any crystal orientation because other twinning systems were easily activated.\(^5\)\(^7\) In contrast, the activation of all kinds of twins could be suppressed in tension in the [205]* orientation.\(^8\)\(^9\) Therefore, the effect of Rh addition on the plastic behaviour by (001)[100] slip was examined in tension in the [205]* orientation.

Figure 8 shows the temperature dependence of the CRSS for (001)[100] slip in Rh-doped ternary and binary Ni_3Nb single crystals deformed in the [205]* orientation in tension.

Figure 8 shows the temperature dependence of the CRSS for slip on (001)[100] in Rh-doped ternary and binary Ni_3Nb single crystals deformed in the [205]* orientation in tension.
marked serrations were observed on the stress-strain curves in the anomalous strengthening temperature range similar to those in binary Ni₃Nb crystals.

Figure 9 shows the dislocation structure in Rh-doped ternary crystals deformed 3% in the [205]∗ orientation at different temperatures. The temperature dependence of the morphology of the dislocation structure is analogous to that in the binary crystal. At 300°C, most dislocations are aligned straight along the [100] screw orientation. At 700°C where significant serrations were observed on the stress-strain curve, the density of screw dislocations decreases. Most dislocations tend to be aligned in a direction along 40–50° away from their screw orientation. This tendency is much stronger than that in binary crystal. A similar dislocation structure is observed at 1000°C.

Figure 10 shows weak-beam images of [100] screw dislocations in binary and Rh-doped ternary crystals deformed in the [205]∗ orientation at 300°C. The [100] dislocation is dissociated into two 1/2[100] superpartials. The average distance of dissociation in the screw segments is 11nm and 24nm in binary and Rh-doped ternary crystals, respectively. This suggests that the APB energy on the (001) plane between two 1/2[100] superpartials is reduced by Rh addition.

4. Discussion

4.1 Effect of Rh addition on CRSS for (010)[100] slip

Rh addition remarkably increased the CRSS for (010)[100] slip around RT and above 800°C, as shown in Fig. 2. The increment of CRSS at low temperatures may be caused by solid-solution hardening. Strong solid-solution hardening by an additional element was also reported in Ni₃Al in which anomalous strengthening occurs due to K-W locking (for example, see16). In some cases solid-solution hardening was effective up to the peak temperature. The addition of alloying elements is believed to affect not only a classical solid-solution behaviour but also leads to a change in activation barrier for the core transformation of superdislocations in the K-W locking process in Ni₃Al-based alloys.17 Thus, the solid-solution hardening behaviour in this type of compound is very complicated. In this study, a remarkable difference in CRSS between binary and Rh-doped ternary Ni₃Nb crystals was observed at around RT, but the difference decreased with increasing temperature and was finally negligible in the range between 500 and 800°C. Similar strong hardening behaviour which occurred only at limited low temperatures was reported in Ni₃Ge-containing Fe.18

Figure 11 shows weak beam dark-field images of [100] dislocations in Rh-doped ternary Ni₃Nb single crystals deformed in the [110]∗ orientation in compression at 700°C. Foils were cut parallel to (011) plane and observed from different beam directions of [010], [101] and [001]. A [100] dislocation is dissociated into two widely-separated 1/2[100] superpartials.
on the (001) plane, which is perpendicular to the (010) slip plane, indicating that it is K-W locked. Such dissociation on (001) was also observed in the binary crystal. As shown in Fig. 10, the dissociation distance between 1/2[100] superpartials on (001) was increased by Rh addition. This clearly indicates that the Rh addition reduces the APB energy on (001). No significant difference in the peak stress between binary and Rh-doped ternary crystals was observed, however, suggesting that the APB energy on the (001) plane is not the only decisive parameter controlling the peak value of anomalous strengthening in this compound. Since dissociated [100] screw dislocations on (010) could not be confirmed in the TEM foils, the APB energy on (010) must be very high in both crystals.

In Rh-doped crystals, a broad anomalous peak was observed between 800 and 1100°C. According to TEM observation, two strengthening mechanisms exist in this temperature range; the motion of screw dislocations controls the plastic deformation between 800 and 1000°C, while edge dislocations play an important role in flow stress between 1000 and 1100°C.

Screw dislocations at 900°C showed very straight morphology similar to those at low temperatures. This suggests that the unlocking stress of screw dislocations in Rh-doped crystals does not decrease rapidly below 1000°C. In the unlocking process of K-W locked screw segments, the constriction of superpartials dissociated on (001) is required, and therefore the mobility of dislocations on (001) may be an important factor in controlling the unlocking stress. For (001)[100] slip, Rh addition shifted the peak temperature to 900°C as shown in Fig. 8 and straight (locked) screw dislocations were observed up to this temperature in specimens deformed in the [110] orientation. Therefore, Rh addition may increase the friction stress for the [100] dislocations on (001) resulting in an increase in the unlocking stress of K-W locked [100] dislocations. The detailed explanation of the increase in the peak temperature for (001)[100] slip by Rh addition is not yet clear, but it may be related to the increase in anomalous strengthening of (001)[100] slip caused by the P-L effect.

In the high temperature range between 1000 and 1100°C where edge dislocations were dominant, high CRSS was maintained. The motion of [100] edge dislocations may be controlled by the climbing process in this temperature range because minimal activation volume was obtained. In binary Ni3Nb, numerous wavy edge dislocations and many dislocation loops were observed. Dislocation loops were aligned in a row along the [001] edge orientation. The wavy dislocation morphology and rows of dislocation loops are strongly related to the frequent climbing process. Phillips et al. suggested a detailed mechanism for the formation of a row of dislocation loops from the fluctuation and subsequent breakup of edge dislocation dipoles involving the self-climbing process. In Rh-doped ternary crystals, edge dislocations were relatively straight and the density of dislocation loops was less than that in binary Ni3Nb. Addition of Rh with high melting point (1964°C) may decrease the inter-diffusion rate in ternary crystals and is effective in improving high-temperature strength because it suppresses the climbing motion of edge dislocations. The effect of alloying elements with high melting point on strength was also reported in Ni3Al crystals deformed near [001] orientation where octahedral slip was still operative even above the peak temperature.

### 4.2 Phase stability and SISF energy in Ni3Nb with D0₉ structure

V addition is thought to change the phase stability of the D0₉ structure with respect to the D0₂₂ structure and to decrease SISF energy in Ni₃Nb. In this case, more (010)[001] slip is activated. The CRSS for (010)[001] slip in this study could not be reduced by V addition, however, and the transition temperature from (010)[100] to (010)[001] slip was not changed by such addition as shown in Fig. 6. The dislocation morphology also did not show a marked difference between binary and V-doped Ni₃Nb crystals. These results imply that the phase stability of the D0₉ structure in Ni₃Nb with respect to the D0₂₂ structure is not effectively changed by V addition.

Hayashi et al. reported that frequent dissociation of [001] dislocation into two very widely-separated superpartials with SISF fringe was observed in Ni₃Ta with the D₀₉ structure. Giessen et al. investigated the phase stability of the D₀₉
structure in some compounds including Ni$_3$Nb and Ni$_3$Ta.\textsuperscript{21)} They demonstrated the crystal structure of Ni$_3$Ta was easily changed from the D0$_\text{a}$ to the D0$_{22}$ structure by cold working, while such a phase transition never occurred in Ni$_3$Nb.\textsuperscript{21)} These reports clearly suggests that the SISF energy in Ni$_3$Ta is considerably lower than that in Ni$_3$Nb, which is in good agreement with the present results. A large amount of Ta addition, therefore, seems to be another candidate which decreases the SISF energy and promotes (010)[001] slip in Ni$_3$Nb.

5. Conclusions

The effect of V and Rh addition on the plastic deformation behaviour in Ni$_3$Nb single crystals with the D0$_\text{a}$ structure was investigated by compressive and tensile tests. The results were summarised and the following conclusions were reached.

(1) V addition does not increase the CRSS for (010)[100] slip at low temperatures but does increase it above the peak temperature of anomalous strengthening, while Rh addition is effective in increasing the CRSS at low and high temperatures. Significant improvement in high temperature strength is achieved by Rh addition.

(2) Strengthening of Ni$_3$Nb by Rh addition at high temperatures is the result of an increase in unlocking stress of K-W locked screw dislocations and the suppression of the climbing motion of edge dislocation due to a decrease in the inter-diffusion kinetics.

(3) Rh addition decreases the APB energy on (001) as we expected. However, no significant difference in the peak stress for (010)[100] slip between binary and Rh-doped ternary crystals appears. This implies the APB energy on the (001) plane is not the only decisive parameter controlling the peak value of anomalous strengthening in Ni$_3$Nb.

(4) Although V addition is expected to enhance (010)[001] slip by reducing the SISF energy created between superpartials, the transition temperature from (010)[100] to (010)[001] slip does not change by V addition. On the other hand, Rh addition raises the transition temperature and increases the CRSS for (010)[001] slip.

(5) Rh addition is effective in increasing the CRSS for (001)[100] slip. The peak temperature of anomalous strengthening is raised 100°C above that in a binary Ni$_3$Nb crystal.

Acknowledgements

This work was supported by a Grant-in-Aid from the Japanese Ministry of Education, Culture, Sports, Science and Technology. This work has partly been carried out at the Strategic Research Base “Handai Frontier Research Center” supported by the Japanese Government’s Special Coordination Fund for Promoting Science and Technology. One of the authors (K.H.) would like to thank the Japan Society for the Promotion of Science (JSPS) for a research fellowship.

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