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Citation	ISIJ International, 29(1), 1-23 https://doi.org/10.2355/isijinternational.29.1
Issue Date	1989-12-15
Doc URL	http://hdl.handle.net/2115/75176
Type	article
File Information	ISIJ Int. 29(1)_ 1-23.pdf



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Plastic Behaviour in $Ni_3(Al,X)$ Single Crystal — Temperature, Strain-rate, Orientation and Composition —

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(Received on July 8, 1988; accepted in the final form on September 9, 1988)

The shear stress data for $L1_2$ single crystals for more than 50 kinds have been already compiled. The fact that the ternary additive is inevitable to facilitate the single crystal growth of Ni_3Al is rather fortunate for us, because its selection is widely different by individual workers, and this situation enables us to evaluate the effect of ternary elements on the plastic behaviour in $Ni_3(Al,X)$ single crystals. Referring to the comprehensive data for polycrystalline $Ni_3(Al,X)$, the solid solution hardening of the CRSS for octahedral slip at low temperatures and the positive temperature dependence of the CRSS for octahedral slip are evaluated mostly on $Ni_3(Al,X)$ single crystals in terms of the effects of compositions including both the deviation from stoichiometry and the ternary additions, and the effect of orientations of the stress axis. Above the temperature showing the maximum strength, the behaviour of the CRSS for cube slip controlled by Peierls mechanism and the CRSS for octahedral slip controlled by viscous motion of dislocations are analysed in terms of the dependent variables of temperature, strain-rate, orientation and compositions. Comparison of the plastic deformation is also extended to other $L1_2$ compounds such as Ni_3Ga , Ni_3Ge , Co_3Ti and Pt_3Al , which exhibit a big contrast each other. Also pointed out is the areas where the future research and development will be needed.

KEY WORDS: defect hardening; solid solution hardening; positive temperature dependence of strength; strain-rate dependence of strength; cube slip; octahedral slip; peak temperature; low temperature sensitivity of strength; tension/compression flow stress asymmetry; offstoichiometry; viscous flow; orientation dependence of strength; Ni_3Ge ; Ni_3Ga ; Ni_3Al ; Pt_3Al ; Co_3Ti ; $L1_2$ compound; $L1_2$ single crystal.

1. Present Status

Gamma prime is anomalous. Because γ' Ni_3Al shows the positive temperature dependence of strength. The flow stress increases rather sharply with increasing temperature, reaching a peak and then decreases. In 1957, this anomaly has been first found in a study on hot hardness by Westbrook,¹⁾ and subsequently confirmed in a study on tensile flow stress by Flinn.²⁾ Such anomaly has been reported in many other $L1_2$ intermetallic compounds; Ni_3Si by Lawrie,³⁾ Co_3Ti by Thornton and Davies,⁴⁾ Ni_3Ga by Takeuchi and Kuramoto,^{5,6)} and Ni_3Ge by Pak *et al.*⁷⁾ A marvel is that nickel base superalloys, being strengthened by the precipitation of γ' , had already been developed and commercialy used at high temperature duties before we have realized this nature of γ' .

Gamma prime is unique. Because γ' Ni_3Al , being one of the Berthollide type compounds, has a relatively wide homogeneity range around stoichiometry in the Ni-Al binary system and in many cases has extended homogeneity lobes into Ni-Al-X ternary systems.⁸⁻¹⁰⁾ That is, γ' Ni_3Al can accommodate a fairly large number of elements, not only transition metal elements but also B-subgroup elements, into its substitutional solid solution,¹¹⁾ resembling the case in nickel.¹²⁾ On account of this feature the γ' single

phase alloys or the γ/γ' two phase alloys are endowed a large capability for modifications by alloying in order to change the properties. It leaves us still big margins to be encouraged to design new nickel base heat-resistant alloys, although a significant amounts of superalloys containing various kinds of solutes have already been developed.

The mechanism based on the so-called Kear-Wilsdorf locks is now accepted to interpret the anomaly in $L1_2$ compounds. The Kear-Wilsdorf mechanism has been furnished in detail on the basis of experiments on plastic deformation of single crystals, the observation of dislocation behaviour by transmission electron microscope and theoretical considerations on dislocation dissociations. Those are to be found in the review papers in detail.¹³⁻¹⁵⁾ Here, it can be stated that the mechanism involves thermally activated cross slip of $1/2[101]$ screw dislocations on (111) primary glide plane to (010) non-glide plane resulting locking of the cross slipped segment to raise the flow stress with increasing temperature. This means that the lowest antiphase boundary (APB) energy on (100) non-glide plane, being intrinsic to the nature of $L1_2$ crystal structure, is a prerequisite for the Kear-Wilsdorf mechanism.^{2,16)}

With the mechanism in mind, a question may arise why not all of $L1_2$ ordered alloys show the anoma-

ly.^{17,18)} The phase stability concept proposed by the group of the present authors could successfully answer this question. The concept is based on a broad survey on the temperature dependence of flow stress in a number of $L1_2$ compounds and it has been shown by them that a lower phase stability of $L1_2$ phase with respect to $D0_{22}$ or $D0_{19}$ phase is responsible for a higher magnitude of the anomalous strength behaviour. Consequently, it has been shown that a systematic variation in phase stability could be achieved by partially replacing one of the components in the compound to result in increasing or decreasing either atomic radius ratio or electron concentration.¹⁹⁻²¹⁾ The concept has yielded in the course many findings of new $L1_2$ compounds having the anomaly but yet has been ignored.^{17,18)} The effect of the compositional deviations from stoichiometry^{22,23)} and the ternary additions²⁴⁻²⁷⁾ on the magnitude of the anomaly in γ' Ni_3Al can also be well explained by this concept.^{28,29)}

Investigations on single crystals of $L1_2$ compounds, most often in Ni_3Al , have extensively been carried out in the past two decades. In order to facilitate the growth of single crystalline Ni_3Al , ternary additions are inevitable to avoid a peritectic reaction during solidification that occurs in the Ni-Al binary system. For the reason, most of the experiments have been performed on ternary systems of the type $Ni_3(Al, X)$. Such situation is, however, rather fortunate. A compilation of these experimental data by itself provides us invaluable information on the effect of alloying elements since individual worker has chosen a different kind of ternary element for the purpose. Among these efforts, noteworthy is a work by Curwick presented in a form of Ph.D dissertation back in 1972.³⁰⁾ His result of the flow stress on single crystalline $Ni_3(Al, X)$ includes the effect of Mo, Nb, Ta, Ti and W, systematically investigated based on the same experimental technique. A similar size of experimental works on single crystalline $Ni_3(Al, X)$ is currently being performed by Heredia and Pope.^{31,32)}

In all the past studies, high temperature flow stress data were taken only to show the existence of the peak but not to interpret the origin of the behaviour. It is really understandable that the most of efforts were dedicated to the study on the anomaly itself and relatively little attention was paid to the temperature regime showing the ordinary negative temperature dependence of strength beyond the peak. However, it is practically important to predict the peak temperature shift by the change in the orientation, strain-rate or composition.

The available shear stress data, especially at elevated temperatures, have been compiled and evaluated by the present authors.^{33,34)} These works are motivated by the recent studies on $Ni_3(Al, Ti)$ single crystals at high temperatures, in which rather good progress has been made in quantitatively rationalizing the effects of the orientation, strain-rate and temperature on the operative slip modes and the peak temperature shift.^{35,36)} Those efforts offer an opportunity to provide a comprehensive understanding on the data reported in the past on the plastic behaviour of $L1_2$

single crystals in the entire temperature range concerned, together with sufficient data on the polycrystalline compounds. This is the intention of the present review.

2. General Aspect

A schematic of the temperature dependence of shear stress resolved onto (111) plane at a fixed strain-rate is shown in Fig. 1, in Ni_3Al single crystals having typical two different orientations of stress axis; one is away from and the other near [001]. Here, we denote the former as the orientation A and the latter the orientation B. The slip system operated is (111)[$\bar{1}01$] in the temperature regime I below the peaks T_{pc} and T_{po} for both the orientations. The peak T_{pc} appears by the onset of cube slip for the orientation A, while the octahedral slip still operates above the peak temperature T_{po} for the orientation B. For this sake, the temperatures showing the peak stress are classified into the categories as T_{pc} and T_{po} , and thus the temperature regimes above the peaks are designated as the regime II and the regime III, respectively. In order to reconcile to the figure presented by the CRSS for (111)[$\bar{1}01$] slip, the CRSS for (001)[$\bar{1}10$] slip in the regime II is divided by the Schmid factor ratio R , where $R = S_c/S_o$ and S_c and S_o are the Schmid factors on (001)[$\bar{1}10$] and (111)[$\bar{1}01$]. (see Appendix) This procedure enables us to make visible the peak temperature T_{pc} , as a cross point of the shear stress curves.

In the regime I, where the octahedral slip is operative, the observed shear stress τ_{oct} is considered as the sum of two terms,^{18-20,22)}

$$\tau_{oct} = \tau_{G(oct)} + \tau'_{oct} \dots\dots\dots(1)$$

where $\tau_{G(oct)}$ has the ordinary negative temperature dependence mostly arising from modulus change with temperature, while τ'_{oct} has the anomalous positive temperature dependence caused by the thermally activated cross slip being well-known as the Kear-Wilsdorf mechanism. For the thermal component τ'_{oct} , a form of Arrhenius-type dependence is immediately suggested,

$$\tau'_{oct} = A_0 \exp(-U/kT) \dots\dots\dots(2)$$

where, A_0 : a temperature independent constant
 U : an apparent activation energy
 k, T : usual meanings.

As a result, the bottom temperature T_b will appear at the condition $\partial\tau_{oct}/\partial T = 0$ and $\tau_{G(oct)}$ becomes $\tau_{0(oct)}$ at absolute zero temperature.^{18-20,22)} The composition and orientation dependences of $\tau_{G(oct)}$ and τ'_{oct} will be discussed in Chaps. 3 to 5.

In the regime II, the observed shear stress τ_{eub} is expressed as the sum of the effective stress τ'_{eub} and the athermal stress $\tau_{G(eub)}$,

$$\tau_{eub} = \tau_{G(eub)} + \tau'_{eub} \dots\dots\dots(3)$$

The deformation mode in this temperature regime characterised by cube slip is considered to be controlled by the Peierls-Nabarro mechanism.³⁵⁾ At the

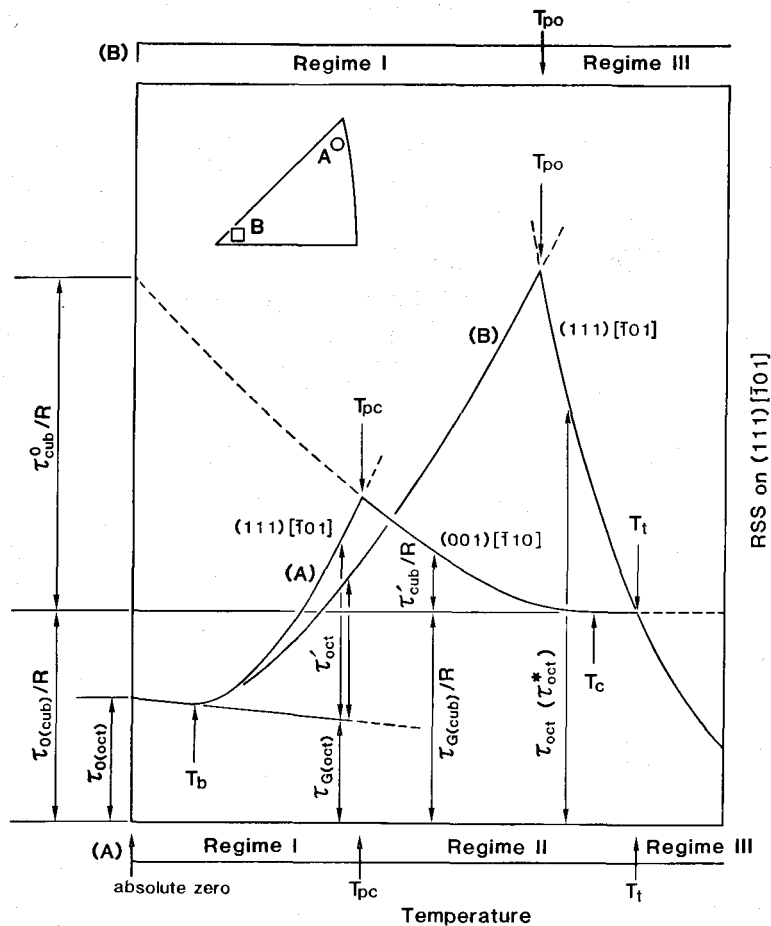


Fig. 1. A schematic illustration of the temperature dependence of shear stress resolved onto (111) plane at a fixed strain rate in Ni_3Al single crystal.

Orientation dependence of the appearance of particular peak temperature is shown for two typical orientations; A being away from and B near [001]. Most of the nomenclatures used in the text are appearing.

critical temperature T_c the stress component τ'_{cub} vanishes and then $\tau_{\text{cub}} = \tau_{G(\text{cub})}$. The temperature and strain-rate dependences of τ'_{cub} will be discussed in Chap. 6. In the chapter, also discussed are the orientation dependence of T_{pc} and the composition dependence of $\tau_{G(\text{cub})}$.

The regime III appears for the specimens having the stress axis near [001]. Because of the very small RSS for cube slip to operate, the regime I is extended up to enough high temperature, where the diffusive or viscous flow can be introduced on the octahedral plane. Thus, T_{po} is strongly dependent on strain-rate. When octahedral slip governs the deformation above T_{po} , a characteristic yield drop and the following steady-state deformation are observed on the stress-strain curve.³⁶⁾ Chapter 6 will be devoted to the formulation of the steady-state stress, τ_{oct}^* , as a function of temperature, strain-rate and compositions.

In Chap. 7, mention will be made on Pt_3Al and Co_3Ti single crystals, which exhibit a marked contrast to nickel base $L1_2$ compounds and provide us more comprehensive understanding on the plastic behaviour of $L1_2$ compounds. In Chap. 8, the discussion will be extended to the transition of the peak temperature from T_{po} to T_{pc} by the change in orientation of the crystals for various kinds of $L1_2$ compounds.

3. Defect Hardening and Solid Solution Hardening

3.1. Offstoichiometry and $\sigma_{G(\text{oct})}$

The effect of compositional deviations from stoichiometry on $\tau_{0(\text{oct})}$ is not known, because of the difficulty in growing the single crystals all over the homogeneity range. The effect, however, would be revealed by the results of the 0.2% flow stress $\sigma_{G(\text{oct})}$ on polycrystalline Ni_3Al . This kind of data have been first reported in hardness by Guard and Westbrook⁸⁾ and later in compressive flow stress at room temperature by many workers.³⁷⁻³⁹⁾ All these results show that the significant hardening takes place for Al-rich deviation but only a small amount of hardening for Ni-rich deviation. In Fig. 2 shown are the change in the 0.2% flow stress at 77 K, $\sigma_{\text{oct}(77)}$, and at room temperature, $\sigma_{\text{oct}(RT)}$ for nickel base $L1_2$ compounds.^{22,23)} Practically, it can be assumed that $\sigma_{\text{oct}(77)} \approx \sigma_{0(\text{oct})}$. It is clear that the asymmetric defect hardening occurs accompanying the minima of strength at stoichiometry, which is a commonly observed characteristic of ordered alloys at low temperatures.^{8,40-42)} This figure shows that on Al- and Ga-rich deviations the flow stress at room temperature is more intense than that at 77 K. This is due to the increased effect of the anomaly with increasing temperature. It is needed to use the flow stress at a temperature as low as possible in order to separate the defect hardening as well as the solid solution hardening from the strength anomaly as stated in

Chap. 2.

In Ni_3Al the point defect caused by the deviations from stoichiometry is not the constitutional vacancies, being found in NiAl and CoAl in the form of unfilled lattice sites by Ni atoms on Al-rich side of stoichiometry.^{8,43,44} Instead of this, the anti-structure defects,^{22,45} where the substitution of excess atoms is for vacant sublattice sites, occurs in Ni_3Al on both sides of stoichiometry. This is confirmed by the facts that the lattice parameter changes continuously beyond stoichiometry,²² the measured density of offstoichiometric alloys is in accord with the calculated value using lattice parameter data⁴⁶ and there is no difference between the diffusion rates for both side of stoichiometry.⁴⁷ NiAl has a nature of electron compounds,⁴⁸ where the constitutional vacancies are formed in such a way as to hold the number of electrons per unit cell constant. On the other hand, in Ni_3Al such is not the case but the electron density of state resembles to that of nickel^{49,50} which is a typical transition metal element.

In order to explain the defect hardening, Aoki and Izumi have tried to apply the Fleischer-type theory on the solid solution hardening.³⁹ However, this attempt is unlikely, because the hardening rates are not the same but the changing rates of lattice parameter are the same in both sides of stoichiometry.²² At present the cause of the defect hardening remains unexplained by the theory, even if we may take into account the effect of elastic modulus change accompanied by the compositional deviations from stoichiometry.⁵¹

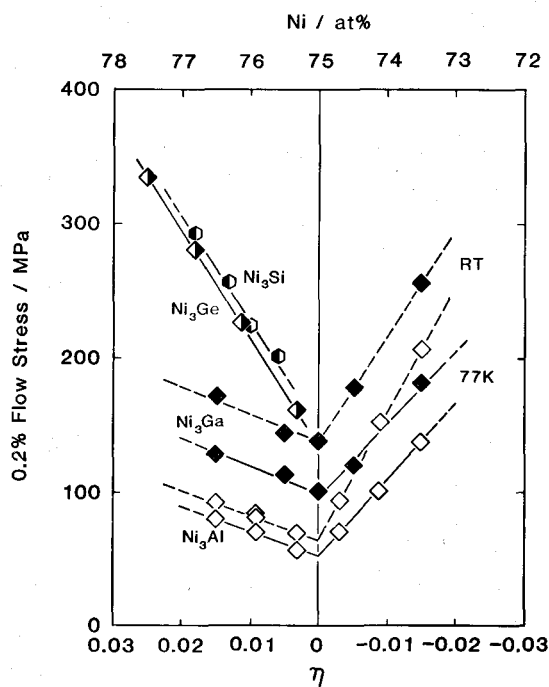


Fig. 2. Effect of the deviation from stoichiometry, expressed by both the Ni concentration and the deviation parameter $\eta = 1/4 - (x + y)$ on the 0.2% flow stress evaluated at 77 K, $\sigma_{\text{oct}(77)}$, and at room temperature, $\sigma_{\text{oct}(RT)}$, for Ni_3Al and Ni_3Ga .²² Also shown are $\sigma_{\text{oct}(77)}$ for Ni_3Si and Ni_3Ge .²³

3.2. Ternary Additions and $\sigma_{G(\text{oct})}$

Pioneer work for the solid solution hardening in Ni_3Al has been done again by Westbrook.¹ Subsequent works on the hardening effect of ternary additions to polycrystalline Ni_3Al have been carried out by Thornton *et al.*,⁵² Lopez and Hancock,³⁷ Rawlings and Staton-Bevan,³⁸ and Aoki and Izumi,³⁹ although a limited number of solute elements were examined. For the analysis in terms of the Fleischer-type elastic interactions, the information of the substitution behaviour, the lattice parameter change and the modulus change by ternary additions are inevitable. The alloying behaviour of Ni_3Al , *i.e.*, whether a certain addition substitutes exclusively for Al, exclusively for Ni or for both sites has been comprehensively evaluated by the group of the present authors.^{9,10} The effort was based on their own experimental works on the direction of the solubility lobe of $L1_2$ phase, together with the available data on ternary phase diagrams including the work first done by Guard and Westbrook.⁸ (see Appendix)

Solid solution hardening of polycrystalline Ni_3Al slightly deviated to Ni-rich side has been investigated by Mishima *et al.*¹¹ for the additions of a variety of both B-subgroup and transition metal elements, all of which substitute for Al-site.⁹ (see Appendix) Referring to the systematic investigation on the rate of lattice parameter change da/dx ⁵³ and that of modulus change dE/dx ,¹¹ various types of elastic interaction between the strain fields of a dislocation and a solute have been examined to analytically describe the hardening. It has been found that the hardening rate $d\sigma_{G(\text{oct})}/dx$ is best described by a combined parameter appropriate for the elastic interaction involving edge dislocations, as has been observed in many other fcc terminal solid solutions.¹¹ Also, it has been found that the atomic size misfit plays a major role and the contribution of the modulus misfit is minimal.^{11,24,25} Thus, the result can be illustrated simply by the rela-

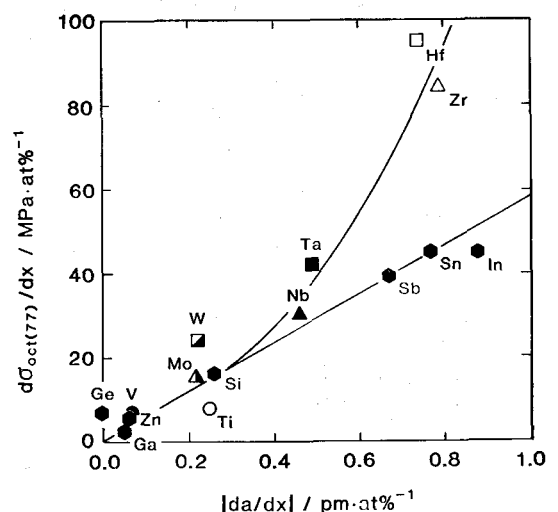


Fig. 3. Relation between the rate of solid solution hardening, $d\sigma_{\text{oct}(77)}/dx$, and that of lattice parameter change, da/dx , with additions of various ternary elements to $\text{Ni}_3(\text{Al}, X)$ polycrystals.¹¹ The composition is slightly deviated to Ni-rich side of stoichiometry and all the ternary elements substitute for Al-site.⁹

tion between $d\sigma_{G(\text{oct})}/dx$ and da/dx , as shown in Fig. 3.²⁵⁾ Obviously, the relation is found to split into two correlation curves, one for transition metal elements and the other for B-subgroup elements. These findings are the same in nature as what is observed in the solid solution hardening of nickel.¹²⁾

It is obvious that there is an extra hardening which can not be explained by the elastic interaction theory for the additions of transition metal elements in Ni_3Al as well as in nickel. It has been concluded that the extra hardening effect arises mainly from characteristic $d-d$ hopping interactions between the host nickel and transition metal solutes, which are essentially absent for B-subgroup solutes having only sp valence.⁵⁴⁾ The reasons why the extra hardening has not been observed clearly until recently are the followings:

(1) the experiments on the solid solution hardening have been focussed mainly on noble metal solvents, to which few transition metal elements are soluble, and

(2) a systematic experimental study on the solution hardening for both types of solutes has not been performed in nickel, even less in Ni_3Al .^{11,12,54)}

3.3. $\tau_{G(\text{oct})}$ in Single Crystals

In order to assess the hardening effect on $\tau_{G(\text{oct})}$,

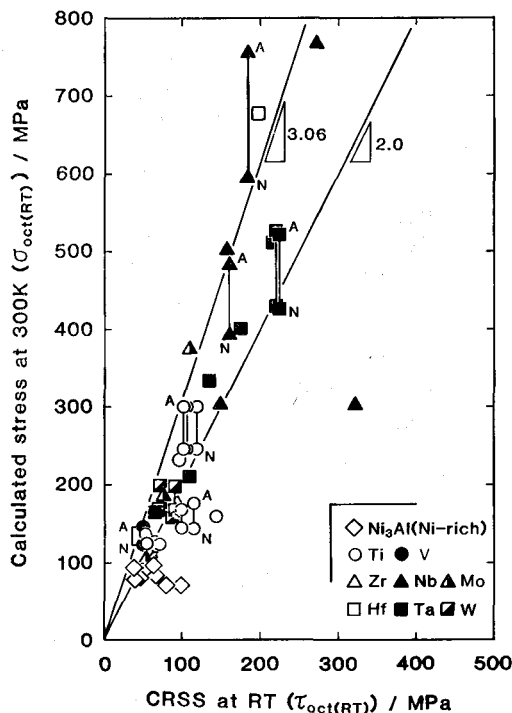


Fig. 4(a).

Relation between the observed CRSS on $(111)[\bar{1}01]$ for $\text{Ni}_3(\text{Al}, X)$ single crystals at room temperature, $\tau_{\text{oct}(\text{RT})}$, and the calculated flow stress for polycrystals of the corresponding compositions, $\sigma_{\text{oct}(\text{RT})}$.⁵⁵⁾ For data being claimed to be at 75 at% Ni, two values can be assigned depending on the extrapolation made from Ni-rich (N) or Al-rich side (A) of offstoichiometry.²²⁾ Two straight lines are drawn with slopes of 3.06, being the Taylor factor, and 2, being the lowest value theoretically derived. There is a good correlation with only one exception of $\text{Ni}_3(\text{Al}, \text{Nb})$.

there are many difficulties such that the characterization and the deviations from stoichiometry of the single crystals were not the same in each experiment and there is uncertainty for estimating the hardening rate on alloying because the binary single crystals as a reference can not be obtained easily. Assuming that $d\sigma_{G(\text{oct})}/dx$ obtained at the binary base composition slightly deviated to Ni-rich side is applicable to any binary composition, *i.e.*, to any offstoichiometric composition, the values of $\sigma_{G(\text{oct})}$ for any ternary polycrystal can be calculated. This assumption implicitly means that X atoms are equally and randomly distributed on the lattice sites instead of Al atoms, where no interaction occurs between them. The comparison between the data for polycrystals and those for single crystals including those provided by Curwick³⁰⁾ and by Heredia and Popc^{31,32)} are made in Figs. 4(a) and 4(b).⁵⁵⁾ Unfortunately, the lowest test temperature employed by Curwick was room temperature. Thus, the comparison is made both for the flow stress at room temperature, $\tau_{\text{oct}(\text{RT})}$, and 77 K, $\tau_{\text{oct}(77)}$, the latter being practically assumed to be nearly equal to $\tau_0(\text{oct})$. In these figures straight lines are drawn to show the Taylor factor being commonly recognized value of 3.06 and the lower limit being the theoretically expected value of 2.0. The systematic relation between $\sigma_{G(\text{oct})}$ and $\tau_{G(\text{oct})}$ is found and the agreement with the lines of the lower bound is quite good.

Electron microscopic observations have shown that dislocations have no pronounced directionality in the

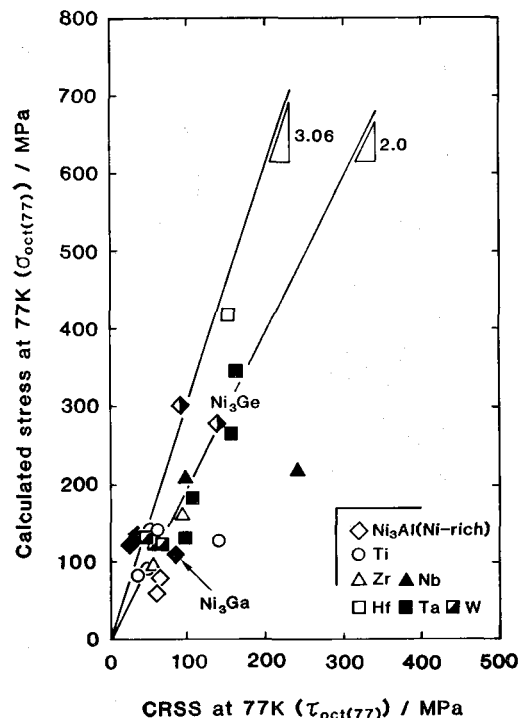


Fig. 4(b).

Relation between the observed CRSS on $(111)[\bar{1}01]$ for $\text{Ni}_3(\text{Al}, X)$ single crystals at 77 K, $\tau_{\text{oct}(77)}$, and the calculated flow stress for polycrystals of the corresponding compositions, $\sigma_{\text{oct}(77)}$.⁵⁵⁾

Being different from Fig. 4(a) the effect of the strength anomaly, and hence N or A marking, is not appearing at this temperature. The observed values for both single- and polycrystals are together shown of Ni_3Ga and Ni_3Ge .

specimens deformed at 77 K, while they are straight being parallel to the Burgers vector and thus consisting of mostly screw character in the specimen deformed above room temperature, where the strength anomaly is predominant.^{15,56-59} It is evident that these observations support the conclusion that the solid solution hardening is governed by the motion of edge dislocations.¹¹ On the other hand, the anomalous temperature dependence of strength is closely related to the mobility of screw dislocations which becomes low compared to that of edge dislocations with increasing temperature. Thus, the assumption of the additivity of the components of flow stress, $\tau_{\text{oct}} = \tau_{G(\text{oct})} + \tau'_{\text{oct}}$, would be rationalized, as shown in Fig. 1. It is recognized that $\tau_{G(\text{oct})}$ is very sensitive to compositions but not strongly sensitive to the strain-rate and orientation. The experimental results agree rather well with the Schmid's Law as is observed in ordinary fcc metals. Deviation occurs only at orientations along the boundaries of the stereographic triangle where the plastic deformation will begin on more than one slip system.

4. Positive Temperature Dependence of Strength (Regime I)

4.1. Temperature Dependence of τ_{oct}

In contrast to the anomalous behaviour of macroscopic flow stress, Ni₃Al is normal on the change with increasing temperature in the microscopic flow stress at $10^{-5} \sim 10^{-6}$ strain^{52,56}) as well as the elastic modulus.⁶⁰ In Fig. 5, the temperature dependence of stress divided by shear modulus, $\tau_{\text{oct}}(T)/G_{\text{oct}}(T)$, being normalized by the value at 4 K is shown for Ni₃Al at the two levels of the flow stress. In the expression, G_{oct} is the shear modulus on the (111) plane in the [110] direction. Together shown are the same quantity for some other L1₂ compounds for comparison.^{56,61,62} Here, the shear modulus data are taken for Ni₃Al, Cu₃Au and Ni₃Fe single crystals provided by Ono and Stern,⁶⁰ Flinn *et al.*,⁶³) and by Turchi

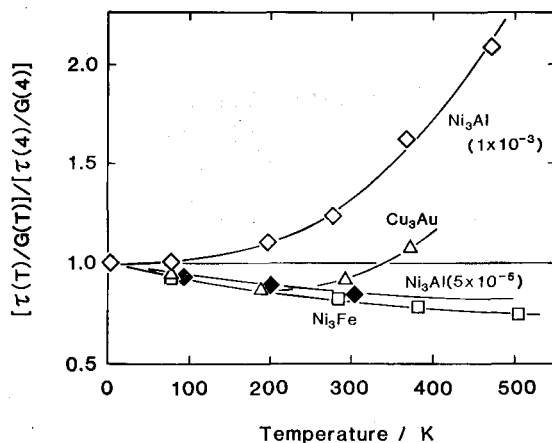


Fig. 5. Temperature dependence of the shear stress at 5×10^{-5} microstrain and 1×10^{-3} strain divided by shear modulus normalized by the value at 4 K in Ni₃Al. Together shown are Ni₃Fe and Cu₃Au ordered alloys; one has no strength anomaly and the other has the strength anomaly.

et al.,⁶⁴) respectively.

Mulford and Pope⁵⁶) have stated that at high temperatures the plastic strain at low stress is related to the motion of edge dislocations and the macroscopic yielding requires that of screw dislocations which is apparently much more difficult. Also, stated is that the loss of mobile edge segments during the initial straining results in a hardening effect on the subsequent loading, which is termed as the microstrain exhaustion. Even in the macroscopic flow in many L1₂ compounds having the strength anomaly, it is often observed, as in Fig. 1, that a normal negative temperature dependence occurs below the temperature T_b .^{5,56} In case of Ni₃Al, T_b is reported to be about 77 K.⁵⁶ In this temperature region, the dislocations are characterized by a random mixture of edge and screw components.⁵⁶⁻⁵⁸

If we could imagine a hypothetical Ni₃Al where the cross slip mechanism of screw dislocations is not activated and no exhaustion hardening takes place, it is a common practice to treat as a weakly negative function of temperature being observed in fcc metals and normal L1₂ compounds, like Ni₃Fe,

$$\tau_{G(\text{oct})} = \tau_{0(\text{oct})}(1 - BT). \quad \dots\dots\dots(4)$$

Referring to Fig. 5, the constant B is defined as $[1 - (G_2/G_1)]/(T_2 - T_1)$ or $[1 - (\tau_1^m/\tau_2^m)]/(T_2 - T_1)$ and then is approximated to be in the range of 0.0003 ~ 0.0004, where τ_i^m is the flow stress at low levels of microstrain at temperature T_i .^{19,20,22} Then, we can determine the thermal component τ'_{oct} by subtracting $\tau_{G(\text{oct})}$ from the applied stress τ_{oct} , as shown in Eq. (1). For the derivation of the thermal component, it has been usually employed as $\tau_{G(\text{oct})} = \tau_{0(\text{oct})} = \text{const.}$ at all temperatures, because of a very small temperature dependence of $\tau_{G(\text{oct})}$. However, we believe that Eq. (4) is much more advantageous because, as shown in Fig. 5, the Cottrell-Stokes ratio tends to reach a lower limit of about 0.7 to 0.8, which is commonly observed values for fcc metals.⁶⁵

4.2. Strength Anomaly and U

Pair dislocations in L1₂ structure are expected to be dissociated into partial dislocations accompanied by various kinds of faults. The types of faults on (111) plane between them are expected to be the antiphase boundary (APB), the superlattice intrinsic stacking fault (SISF), the complex stacking fault (CSF) and superlattice extrinsic stacking fault (SESF). Among them, some of faults have been confirmed by electron microscope and the others not. Stability of possible dislocation dissociations^{58,66-69}) and dislocation core structures⁷⁰⁻⁷²) are theoretically discussed by many workers and details are reviewed by Pope and Ezz.¹⁴ Here, we can simply state that an empirical activation energy U in Eq. (2) is associated with the construction of partial dislocations on (111) plane, which is essential for the cross slip onto (001) plane to occur and that the driving force for cross slip originates from an anisotropy of APB energy, *i.e.*, a very low APB energy on non-glide (100) plane compared to that on glide (111) plane in Ni₃Al.^{2,16})

Based on the thermally activated cross slip model,

Takeuchi and Kuramoto have first expressed their results of τ'_{ot} for Ni_3Ga single crystals by the Arrhenius equation.⁶⁾ The magnitude of the mechanical anomaly can be described by the value of activation energy U . Incidentally, it has been shown that the bottom temperature T_b is a good index to evaluate the activation energy U , in such $L1_2$ compound that the temperature range from T_b to T_{pc} is too narrow to estimate U by the ordinary Arrhenius plot.¹⁸⁾ Cu_3Au , where the disordering takes place about 600 K is a typical example. It can be stated that Cu_3Au is one of the anomalous compounds having a weaker positive temperature dependence of strength than Ni_3Al , as shown in Fig. 2. The activation energy estimated from T_b and $\tau_{0(\text{ot})}$ is 16 kJ/mol.^{21,61)} This value is compared to that for Ni_3Al being 7~8 kJ/mol.

The strain-rate sensitivity for the CRSS for (111) $[\bar{1}01]$ slip, τ'_{ot} , has been frequently reported to be very little as in ordinary fcc metals.^{6,52,65,73-76)}

4.3. Offstoichiometry and U

The activation energy U strongly depends on compositions, *i.e.*, the deviation from stoichiometry and ternary additions. It has been qualitatively known that the positive temperature dependence of strength is greater for Al-rich deviation than for Ni-rich deviation in polycrystalline Ni_3Al .^{8,37-39)} Such tendency that the strength anomaly becomes stronger with increasing the minority component has been also observed in Ni_3Ga ,²²⁾ Ni_3Si ,²³⁾ and Ni_3Ge .²³⁾ Recently, the quantitative evaluation on polycrystalline Ni_3Al has been presented by Noguchi *et al.*,²²⁾ as shown in Fig. 6. In this figure, the effect of deviations from stoichiometry on the activation energy U is shown with the discontinuous fashion at stoichiometry for both binary Ni_3Al and Ni_3Ga alloys²²⁾ and ternary $\text{Ni}_3(\text{Al}, \text{Ti})$ alloys.^{22,37)} Also shown is that Al-rich deviation tends to have a much smaller U and a somewhat larger composition dependence of U than Ni-rich deviation.

Those tendencies have been interpreted on the basis of the phase stability concept.²²⁾ According to this concept, the phase stability of $L1_2$ phase with respect to DO_{22} phase is the origin of the strength anomaly, which results in almost zero APB energy on cube plane and facilitates the thermally activated cross slip of screw segments onto cube plane. It is not easy to prove it directly in the present case of Ni_3Al . However, a broad survey of a number of binary phase diagrams containing $L1_2$ phase shows that the phase transitions are often found from $L1_2$ phase to DO_{22} - or DO_{19} -type phase with increasing the minority component across the A_3B stoichiometry.

4.4. Ternary Additions and U

Phase stability of $L1_2$ phase, which affects the strength anomaly, can well be varied by the additions of ternary elements. It is possible to control the strength anomaly of $L1_2$ compounds by a proper choice of the third element, in either direction whether it is strengthened or weakened. Several typical examples are cited here. It has been shown that by

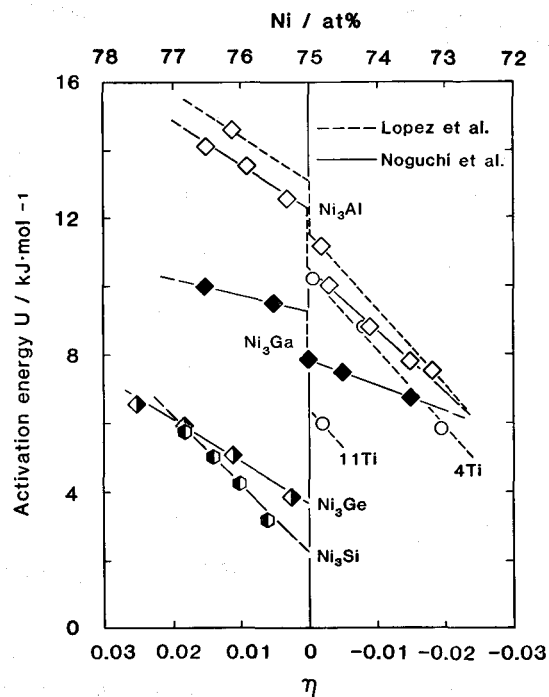


Fig. 6. Effect of the deviations from stoichiometry, expressed by both the Ni concentration and the deviation parameter $\eta = 1/4 - (x + y)$ on the activation energy U for the thermally activated cross slip to yield the mechanical anomaly in Ni_3Al ¹⁹⁾ and $\text{Ni}_3(\text{Al}, \text{Ti})$.²⁴⁾ Together shown are those for Ni_3Ga ,²²⁾ Ni_3Si ,²³⁾ and Ni_3Ge .²³⁾

the substitution of a small amount of Zn for Al the anomaly of Ni_3Al dramatically vanishes²⁶⁾ and that by the substitution of Fe for Ni to form $(\text{Ni}, \text{Fe})_3\text{Ge}$ the anomaly of Ni_3Ge is reduced and finally vanishes with further increase in the substitution ratio.¹⁹⁾ Also, it has been shown that the Ti addition increases the increasing rate of flow stress with increasing temperature.³⁷⁾ This is shown in Fig. 6, where $\text{Ni}_3(\text{Al}, \text{Ti})$ alloys have lower activation energy than Ni_3Al binary alloys. Subsequent to the hot hardness experiment done by Guard and Westbrook,⁸⁾ the compositional effects on the mechanical anomaly for polycrystalline Ni_3Al have been reported by many workers.^{38,39,52)}

For polycrystalline Ni_3Al slightly deviated to Ni-rich side the most comprehensive study of the effect of composition on the strength anomaly, which is qualitatively defined by the activation energy U , has been performed by Ochiai *et al.*^{24,25)} The result is shown in Fig. 7, where the changing rate of activation energy per 1 at% of ternary elements, dU/dx , is related to the changing rate of lattice parameter of 1 at%, da/dx , with the equi-valency contours determined thereby as indices of the valence of B-subgroup elements. From this figure, these noticeable facts can be seen as follows;

(1) the drastic reduction in dU/dx , *i.e.*, the enhancement of the strength anomaly, occurs by changing the ternary solute from 2B- to 4B-subgroup elements at an almost constant atomic radius (from Zn, Ga to Ge),

(2) the reduction in dU/dx is enhanced by the addition of an element with larger atomic size at a

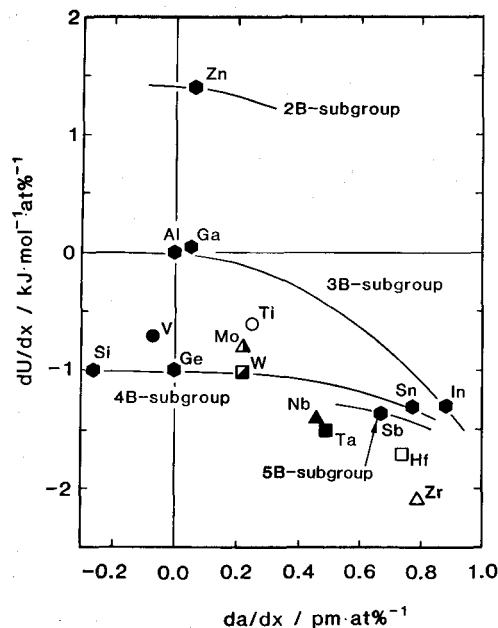


Fig. 7. Relation between the change in activation energy, dU/dx , and that in lattice parameter, da/dx , in ternary $Ni_3(Al, X)$ polycrystals.^{24,25)} Equi-valence contours based on the valence of B-subgroup elements are drawn.

fixed valence (from Ga to In), and

(3) for a transition metal it can be assigned the apparent valence from the effect on dU/dx . In view of the valence effect found in Fig. 7, a large valence would be assigned with decreasing group number for transition metals of 5th (from Mo, Nb to Zr) and 6th (from W, Ta to Hf) periods.

Should be referred here is the effect of those ternary elements on the mechanical anomaly which substitute for the majority component in $L1_2$ compounds. Unfortunately, no work has been done on $(Ni, X)_3Al$ single crystals. From the results of the limited number of experimental works on $(Ni, Co)_3Ge$ single crystals^{77,78)} and $(Ni, Fe)_3Ge$ polycrystals,¹⁹⁾ the following sequence is found on the degree of the mechanical anomaly or the activation energy U ; $U((Ni, Fe)_3Ge) > U((Ni, Co)_3Ge) \geq U(Ni_3Ge)$. This sequence clearly demonstrates the effect of the electron concentrations on the degree of activation energy for the cross slip and is in accord with the phase stability concept. It can be said that with increasing the electron atom ratio by the replacement of a portion of the majority component, the mechanical anomaly becomes intense in the compounds. In this regard, it has been confirmed that both Fe and Co substitute for Ni-site in Ni_3Ge .^{9,19)}

As often stated above, the phase stability of $L1_2$ phase against $D0_{22}$ phase is lowered by the substitution of such ternary elements that reduce the average electron atom ratio or increase the atomic radius ratio.¹⁷⁻²¹⁾ There is a direct evidence to show this criterion. In Kurnakov compounds APB domains are formed below the order-disorder transition temperature. The morphology of APB domains is classified into two types; the swirl-like domains typically found in Ni_3Fe and maze-like domains found in

Cu_3Au .^{21,79,80)} The low APB energy on (100) planes characterized by the maze-like morphology in Cu_3Au is related to its mechanical anomaly. It has been shown that by the addition of small amount of Ni to Cu_3Au , which reduces the average electron atom ratio, the long period superlattice being related to $D0_{22}$ phase becomes unstable, the maze-like morphology converts to the swirl-like and the mechanical anomaly is removed.²¹⁾ In case of Berthollide type compounds, no APB domains are usually formed. However, it has been recently pointed out by Cahn *et al.*⁸¹⁾ that the order-disorder transition temperature crosses over the liquidus temperature, alloys containing less than 23 at% Al freeze in disordered form and order on further cooling. The maze-like domains along (100) planes are often reported in melt quenched Ni_3Al alloys⁸²⁻⁸⁴⁾ in accord with the phase stability concept. Details on the phase stability of $L1_2$ compounds are found in the previous papers.^{22,23,28,29)}

Regarding the constant A_0 in Eq. (2), very little information is available. However, it may be worthwhile to mention that A_0 is weakly dependent on composition.⁸⁵⁾

4.5. Orientation and U (N -dependence)

On Ni_3Ga single crystals, Takeuchi and Kuramoto⁶⁾ have shown that the rate of increase in τ_{oct} with increasing temperature becomes more intense as the compression axis is moved away from [001] direction, *i.e.*, the Schmid factor ratio N is increased, where $N = S_n/S_o$ and S_n and S_o are the Schmid factors on (010)[$\bar{1}01$] and (111)[$\bar{1}01$]. (see Appendix) Schematically, this is shown in Fig. 1, as the difference of flow stress between the orientations A and B in the regime I. Later, similar orientation dependence, as is called the N -dependence, has been confirmed on various kinds of $Ni_3(Al, X)$ by many workers,⁸⁶⁻⁸⁹⁾ on Ni_3Ge by Pak *et al.*,^{77,78)} and on Cu_3Au with weak response by Kuramoto and Pope.⁶²⁾ This behaviour can easily be explained by the cross slip model. For a given shear stress on (111)[$\bar{1}01$], the shear stress on (010)[$\bar{1}01$] being increased with increasing N -value facilitates the cross slip of $1/2[\bar{1}01]$ screw dislocations onto (010) plane. Thus the activation energy U decreases for high value of N .

Takeuchi and Kuramoto⁶⁾ have explained the N -dependence on the activation energy U , giving

$$U = U_1 - A_1 N \tau_{oct}, \dots\dots\dots(5)$$

where, U_1, A_1 : constants for a given composition

$N \tau_{oct}$: the RSS on (010)[$\bar{1}01$].

Equation (5) indicates that the stress $N \tau_{oct}$ which enhances the cross slip from (111) to (010) planes reduces the activation energy U and that the second term naturally leads to a breakdown of Schmid's law at higher temperatures. Fig. 8, for several examples, clearly shows such effect in $Ni_3(Al, W)$,⁸⁶⁾ $Ni_3(Al, Ta)$,⁷⁴⁾ and Ni_3Ge ⁷⁷⁾ single crystals with the relation between U and N .⁸⁵⁾ On this figure it can be recognized that the N -dependence of U is considered to be almost same for all nickel base $L1_2$ compound.⁸⁵⁾

In the past works, the N -dependence of strength

$$\Delta U = (dU/dx)x \dots\dots\dots(7)$$

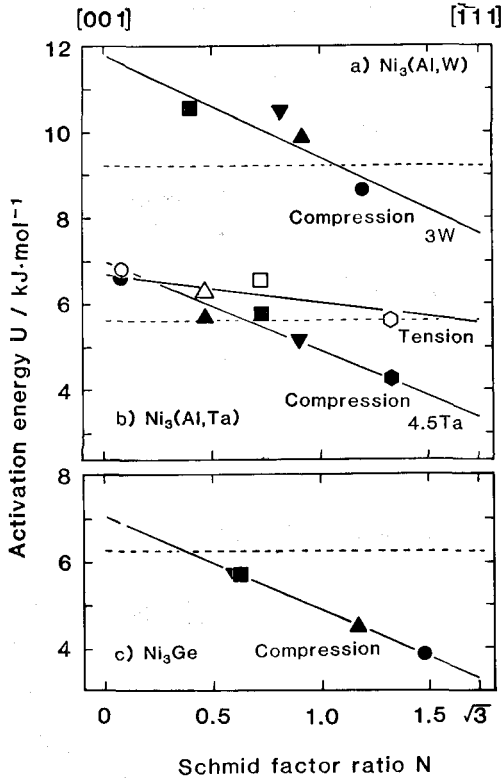


Fig. 8. Orientation dependence, the N -dependence, of the activation energy, U , for (a) $\text{Ni}_3(\text{Al}, \text{W})$,⁸⁶⁾ (b) $\text{Ni}_3(\text{Al}, \text{Ta})$,⁷⁴⁾ and (c) Ni_3Ge .⁷⁷⁾

The dotted line in each figure indicates the calculated value for a polycrystal with the corresponding composition.

In (b), a comparison can be made of the values obtained by tension and compression tests, where the Q -dependence can be seen.

anomaly has most often been presented by the relation between the peak temperature, T_{p0} or T_{pc} , and N -value. It is, however, likely to be inappropriate because the appearance of the peak temperature is controlled by the competition of the operative slip systems as discussed in Chap. 2, but not directly by N -value. It will be shown in Chap. 8 that the peak temperature is better correlated with R -value rather than N -value.

4.6. U for Single Crystals

Comparison can be made between the activation energies for polycrystals and single crystals, under such assumption that is applied to the estimation of $\tau_{\sigma(\text{oct})}$ in Chap. 3. From the result of Fig. 6, the effect of deviations from stoichiometry on U is described as,

$$\begin{aligned} \Delta U &= [(dU/d\eta)_{\eta=+0}]\eta && \text{for Ni rich deviation} \\ \Delta U &= [(dU/d\eta)_{\eta=-0}]\eta && \text{for Al rich deviation} \end{aligned} \dots\dots\dots(6)$$

where, $\eta = 1/4 - (x + y)$

y : the mole fractions of Al

x : the ternary solute X substituting for Al site.

From the result of Fig. 7, the effect of ternary additions on U is described as,

Combining Eqs. (6) and (7), we can calculate the activation energy for polycrystalline $\text{Ni}_3(\text{Al}, X)$, U_{poly} , corresponding to a composition of any single crystal treated.

The activation energy U deduced from the reported values for single crystals are compared with the calculated values of U_{poly} for polycrystals.⁸⁵⁾ Instead of directly comparing U , $f(U) = \exp(-U/RT)$ is here defined and evaluated at 1 000 K as a measure for the contribution of U to the thermal component of the shear or flow stress. The comparison is then made in Fig. 9. Here, the values for single crystals are chosen for two orientations; one for near [001] with smaller N -value and the other for near [111] with larger N -value. In this case, the scatter in the data is inevitable, because of the different characterization of single crystals by individual workers, slightly different orientations of single crystals each other, ignoring of the Q -dependence and a simple assumption for the estimation of U_{poly} on polycrystals. In spite of such several uncertainties, it is rather surprising that there is a good agreement between them. Moreover one can find a clear indication of the N -dependence of U in single crystals by a comparison of Figs. 9(a) and 9(b).

5. Tension/Compression Flow Stress Asymmetry (Q -dependence)

Flow stress resolved on primary octahedral slip plane in the regime II is often observed unequal depending on the sense of the applied stress.^{74,90-93)} As is shown in Fig. 10 for the case of Ni_3Ga ,⁹²⁾ the appearance of this tension/compression asymmetry also depends on orientations in the unit triangle but it can not be explained by the variation in N -value. Pope's group^{74,90-93)} has then introduced another orientation factor termed Q -value, where $Q = S_q/S_o$ and S_q and S_o are the Schmid factor on (111)[121] and that on (111)[101]. (see Appendix) Because $1/2[101]$ screw dislocations in the compound are most probably dissociated into $1/6[\bar{1}\bar{1}2]$ Schockley partials, any stress component that aids their constriction would promote cross slip and *vice versa*. Therefore it is expected that the sign of the RSS on (111) along [121] would decide whether the superpartials are constricted or extended and at $Q=0$ the asymmetry would disappear. This is the criterion first proposed by Lall *et al.*⁹⁰⁾ Thus, the activation energy U including both N - and Q -dependences should be written as,

$$U = U_1 - A_1 N \tau_{\text{oct}} - A_2 Q \tau_{\text{oct}} \dots\dots\dots(8)$$

where, A_2 : a constant.

This model, however, can not explain the fact that the orientation where the asymmetry vanishes is deviated toward [001] side in the unit triangle from the [012]-[113] great circle on which $Q=0$. (see Appendix) Paider *et al.*⁹³⁾ have shown that energetically the most favourable configuration for the cross slip would be such that the core of $1/2[101]$ dislocations is constricted by the applied stress on (111) and is

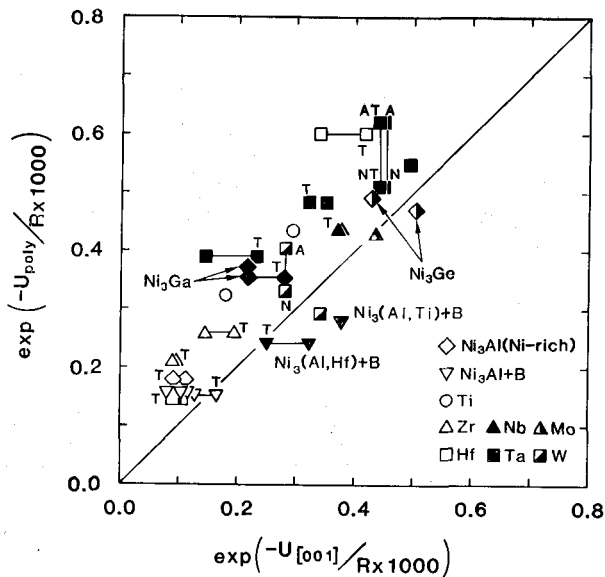


Fig. 9(a).

Comparison between the observed activation energy, U , in single crystalline $Ni_3(Al, X)$ with orientations near $[001]$ and the calculated values, U_{poly} , for polycrystals of the corresponding compositions.⁸⁵⁾

Instead of directly comparing U , $f(U) = \exp(-U/RT)$ is defined and evaluated at 1000 K as a measure for the contribution of U to the thermal component of the shear or flow stress. Together shown are the results for Ni_3Ga and Ni_3Ge .

In case when the composition of single crystal is simply claimed to be 75 at% Ni, two values for a polycrystal are obtained according to whether the extrapolation is made from Ni-rich side (N) or from Al-rich side (A), as shown in Fig. 6. When the test is carried out in tension the data is shown with "T", otherwise the test is in compression.

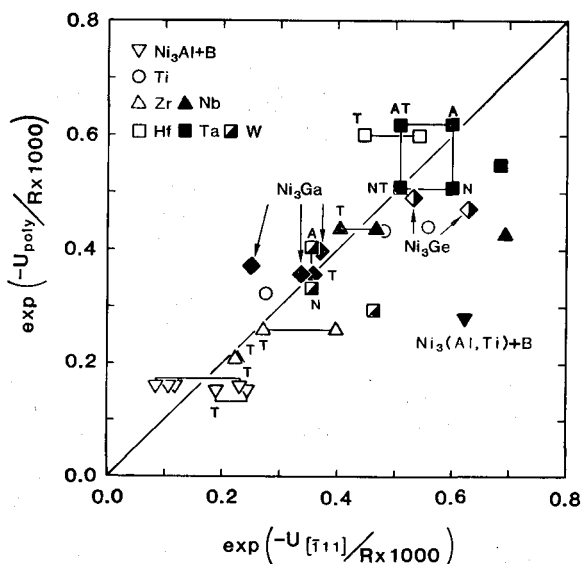


Fig. 9(b).

A similar comparison between observed activation energy, U , in single crystalline $Ni_3(Al, X)$ with orientations near $[111]$ and calculated values, U_{poly} , for polycrystals of corresponding compositions.⁸⁵⁾

extended by that on (111) . The treatment is based on the original work by Escaig.⁹⁴⁾ The model, being called as Escaig model, tells us that any stress component that enhance the dissociation of superpartials

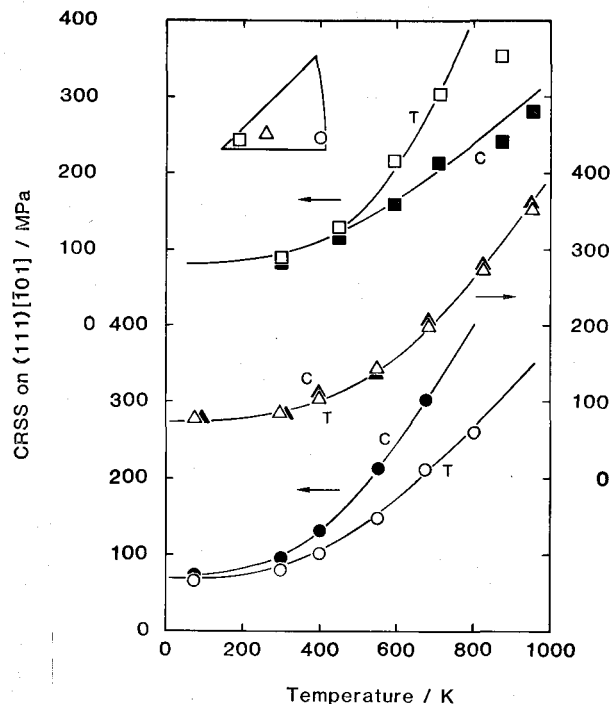


Fig. 10. Temperature dependence of the CRSS on $(111)[\bar{1}01]$ in Ni_3Ga single crystals with three different $[\bar{1}01]$ in Ni_3Ga single crystals with three different stress axis,⁹²⁾ showing tension (T)/compression (C) asymmetry occurring according to the Q -value. (see Appendix)

after the cross slip would stabilize the configuration and thereby raise the flow stress. The sign of the Schmid factor on $(111)[121]$ then become important in addition to N - and Q -values in understanding the tension/compression asymmetry. It has been shown that this new factor changes its sign on $[011]-[\bar{1}12]$ great circle in the unit triangle. (see Appendix) Then the zero-asymmetry boundary has been shown to deviate toward $[001]$ side, by combining the effect of Q -value with this criterion and by considering the change in relative spacing of Schockley partials with sign of the applied stress.⁹¹⁾ The tension/compression asymmetry has also been reported on the single crystals of nickel-base alloys with high volume fractions of γ' .⁹⁵⁻⁹⁷⁾

Detailed analysis and explanation on this phenomenon is best summarized in a review paper by Pope and Ezz.¹⁴⁾

6. Flow Stress above the Peak Temperatures

6.1. Onset of Cube Slip (Regime II)

From the slip trace analysis of deformed Ni_3Al single crystals, Copley and Kear⁶⁶⁾ have found that in the regime II above the peak temperature T_{pc} the slip system operated is $(001)[\bar{1}10]$. This observation has been later confirmed by many workers^{6,35,52,78,98)} in most of $L1_2$ compounds having the mechanical anomaly.³³⁾ Not much work, on the other hand, has been done on the deformation mechanism by cube slip system. Thornton *et al.*⁵²⁾ have shown that the strain-rate sensitivity of the flow stress for $(001)[\bar{1}10]$ slip is very large in Ni_3Al , whereas that for $(111)[\bar{1}01]$

is small as in ordinary fcc metals. Similar observation has been made for Ni₃Ga by Takeuchi and Kuramoto,⁶⁾ for Ni₃(Al, X) by Leverant *et al.*⁷⁶⁾ and Travina *et al.*⁷³⁾ The temperature and strain-rate dependences of the CRSS for (001)[101] slip are shown in Fig. 11, where the data for Ni₃(Al, Ti) containing 5.0 at% Ti are obtained by Miura *et al.*³⁵⁾ and those for Ni₃(Al, Ta) containing 4.5 at% Ta by Umakoshi *et al.*⁷⁴⁾ It can be seen from this figure that the applied stress τ_{cub} could be expressed by Eq. (3) in the regime II, which is characterized by the negative temperature dependence of strength. Also can be seen is that τ_{cub} obeys the Schmid's law. Here, the athermal component $\tau_{G(\text{cub})}$'s are estimated to be 170 MPa for Ni₃(Al, Ti) and 195 MPa for Ni₃(Al, Ta). It will be shown later, however, that the difference in the values is not a direct reflection of the different kinds of ternary element.

The similarity of the temperature and strain-rate dependences of the effective stress observed in bcc metals suggests that cube glide in Ni₃Al is controlled by a thermally activated process. Miura *et al.*³⁵⁾ have shown that the strain-rate is given by

$$\dot{\gamma} = \dot{\gamma}_c \exp(-H/RT) \quad \dots\dots\dots(9)$$

- where, $\dot{\gamma}$: the shear strain-rate
- $\dot{\gamma}_c$: constant
- H : the additional energy that must be supplied by thermal fluctuation to overcome the innate lattice resistance to dislocation motion or the Peierls stress.

Then it follows that

$$H = -k(\partial \ln \dot{\gamma} / \partial T^{-1})_{\tau_{\text{cub}}}$$

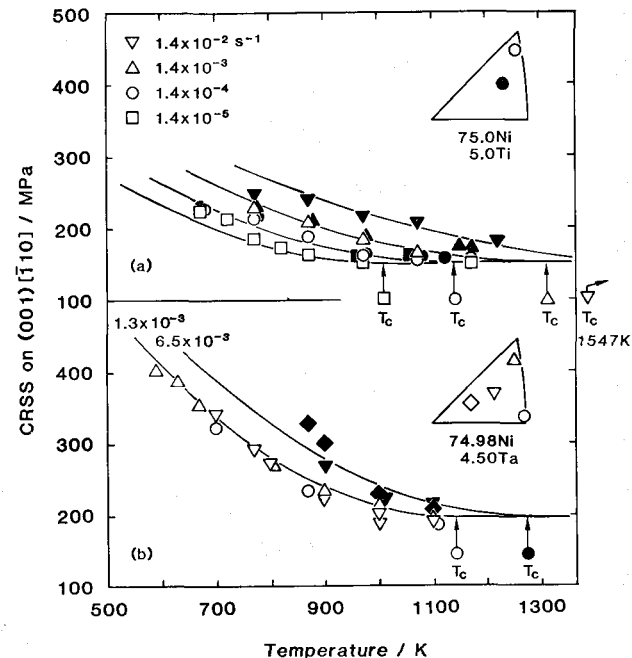


Fig. 11. The temperature dependence of the CRSS for (001)[110] slip, τ_{cub} , at different strain-rates in (a) Ni₃(Al, Ti)³⁵⁾ and (b) Ni₃(Al, Ta).⁷⁴⁾ The critical temperature, T_c , is here defined as the temperature at which the CRSS becomes independent.

$$= -kT^2(\partial \tau'_{\text{cub}} / \partial T) \dot{\gamma} (\partial \ln \dot{\gamma} / \partial \tau'_{\text{cub}})_T \quad \dots\dots\dots(10)$$

$$v^* = -(\partial H / \partial \tau'_{\text{cub}})_T = kT (\partial \ln \dot{\gamma} / \partial \tau'_{\text{cub}})_T \quad \dots\dots\dots(11)$$

The activation energy H and the activation volume v^* is principally a function of the stress and offers some check on the validity of the analysis as a thermally activated process. For Ni₃(Al, Ti) single crystals, the maximum activation energy derived from Eq. (10) is 170 kJ/mol and the activation volume above the effective stress of 10 MPa derived from Eq. (11) is of the order of 5 to 15 \mathbf{b}^3 , where \mathbf{b} is the Burgers vector. The derived activation energy is much smaller than that for inter-diffusion in Ni₃Al. Then the following state equation for the plastic deformation in the regime II is obtained,

$$\tau_{\text{cub}} = \tau_{G(\text{cub})} + \tau_{\text{cub}}^0 [1 - T/T_c]^2 \quad \text{and} \\ 1/T_c = -k/H_0 \ln(\dot{\gamma}/\dot{\gamma}_c) \quad \dots\dots\dots(12)$$

or

$$\tau_{\text{cub}} = \tau_{G(\text{cub})} + [\sqrt{\tau_{\text{cub}}^0} + kT/2Ab^3 \cdot \ln(\dot{\gamma}/\dot{\gamma}_c)]^2, \quad \dots\dots\dots(13)$$

- where, H_0 : the activation energy at $\tau'_{\text{cub}}=0$
- T_c : the critical temperature at which the CRSS becomes independent at a constant strain-rate.

An important conclusion is suggested by the small value of the activation volume derived. The CRSS of cube slip is rate-determined by the Peierls-Nabarro mechanism.³⁵⁾

The composition dependence of $\tau_{G(\text{cub})}$, which is independent on strain-rate can be compared for each result of single crystal experiments. This is done in Fig. 12 as a function of the deviation from stoichiometry.^{33,99)} Although there is a relatively large scatter, it seems that the athermal component $\tau_{G(\text{cub})}$ is not so much affected by the ternary additions but by the deviations from stoichiometry. In other words, the solid solution hardening of $\tau_{G(\text{cub})}$ is small compared to that of $\tau_{G(\text{oct})}$. This trend is mostly emphasized in case of the single crystals containing B, which is soluble interstitially in Ni₃Al. It is recognized on the work done by Heredia³²⁾ the solution hardening rate of $\tau_{G(\text{oct})}$ is considerably increased but that of $\tau_{G(\text{cub})}$ is remained almost constant by the addition of B in Ni₃Al, as shown in Fig. 12. It is interesting to note that among nickel base $L1_2$ compounds $\tau_{G(\text{cub})}$ of Ni₃Ge is relatively high compared to that of Ni₃Al or Ni₃Ga, as seen in Fig. 12.³³⁾ Nevertheless, Pak *et al.*^{77,78)} have shown in Ni₃Ge that T_{pc} is extremely low to be less than 300 K for the specimen having an orientation close to [111]. It is obvious that τ_{cub} easily comes below τ_{oct} because of low T_c of cube slip system in Ni₃Ge and this results in the onset of cube slip at relatively low temperature. This will be mentioned again in Chap. 8.

In the regime II, where the deformation is controlled by cube slip, it has been observed that dislocations have no distinct directionality,^{6,52,77)} and also observed in *in situ* experiments is that the movement of dislocations is steady and continuous,⁵⁹⁾ keeping the separation of unit dislocations almost constant.¹⁵⁾

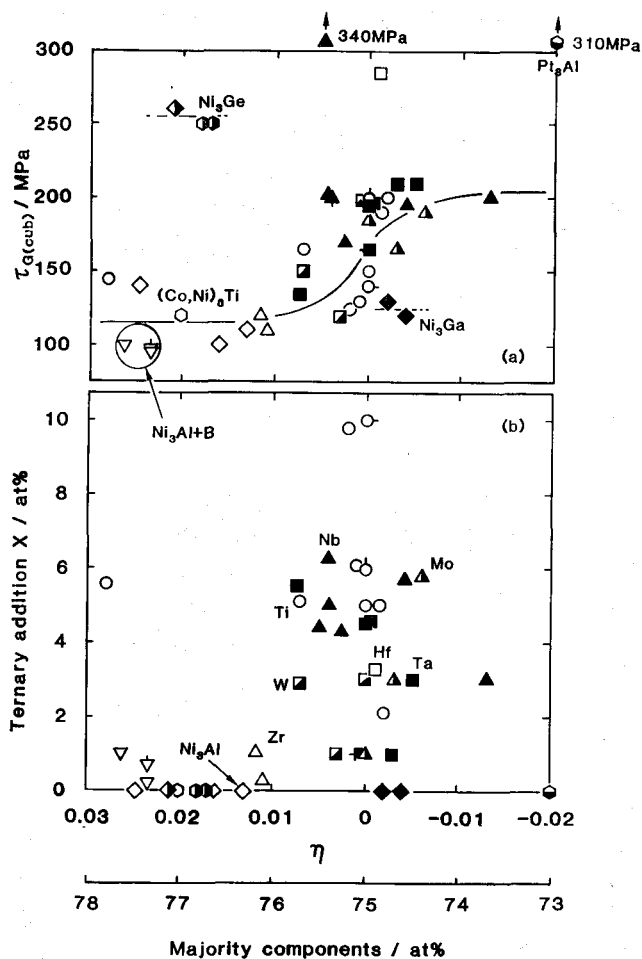


Fig. 12. In (a) is shown effect of composition on $\tau_{G(cub)}$ being the athermal component of τ_{cub} as a function of the deviation from stoichiometry/Ni concentration.⁹⁹⁾ The deviation parameter is so defined as,

$$\eta = 1/4 - (x + y),$$

where x, y : the mole fractions of ternary element X and Al, respectively.

Note that the data for $\text{Ni}_3(\text{Al, Nb})$ being 340 MPa seems to be erratic.

The concentration of ternary element is shown in (b).

This feature strongly suggests again the Peierls mechanism controls cube glide. In contrast to cube glide the dislocation motion on (111) plane is reported to be too fast to observe moving state.^{15,59)}

Unfortunately few works on the strain-rate dependence of flow stress in $L1_2$ single crystals have been done. The composition dependence of the other sets of parameters in Ni_3Al , τ_{cub}^0 , T_c , H_0 , and $\dot{\gamma}_c$, can not be deduced. More experimental and theoretical research works are needed in this area of the regime II.

6.2. Onset of Viscous Flow (Regime III)

There observed many evidences³⁴⁾ to show that octahedral slip still governs the plastic behaviour in the regime III if the stress axis is oriented near [001].^{6,52,66,78,98)} Ochiai *et al.*³⁶⁾ have shown in $\text{Ni}_3(\text{Al, Ti})$ that stress-strain curves for such situation are

characterized by a substantial yield drop and the following steady-state deformation as shown in Fig. 13. In the past works the stress-strain curves as primitive data have not usually been reported and this interesting phenomenon seems to have been overlooked. We can, however, find the yield drop on the stress-strain curves^{66,86,89)} or a negative work hardening rate¹⁰⁰⁻¹⁰²⁾ for the orientation being close to [001] by a careful look in a few previous papers. As shown in Fig. 13, at a temperature just above T_{pc} the yield drop is minimal showing no appreciable work hardening and with further increase in temperature it becomes intense. Such yield behaviour is suggested to be very similar to that of Johnston-Gilman type.³⁶⁾

The CRSS for (111)[101] at the steady state deformation, τ_{oct}^* , decreases with increasing temperature and exhibits normal strain-rate sensitivity which is in strong contrast to τ_{oct} in the regime I. It has been shown that the state equation for τ_{oct}^* can be expressed as,

$$\dot{\gamma} = \dot{\gamma}_0 (\tau_{oct}^*)^n \exp(-E/kT) \dots\dots\dots(14)$$

where, $\dot{\gamma}_0$: a constant

n : the stress exponent.

The expression is similar to that for the diffusion controlled creep and thus implies that the deformation in this temperature regime is a type of viscous flow rate-controlled by diffusion.^{2,103)} The stress exponent n has been estimated to be 3 in this case.³⁶⁾ In case of the steady-state creep on polycrystalline Ni_3Al , the exponent n has been reported to be 2.56⁹⁹⁾ and 3.²⁾ The apparent activation energy for the deformation, E , has then estimated to be ca. 290 kJ/mol, which is of the same order as that found for creep of polycrystalline Ni_3Al being 317¹⁰³⁾ or 326 kJ/mol.²⁾ The value is also comparable with that for inter-diffusion in Ni_3Al ¹⁰⁴⁾ or the self-diffusion of Al in nickel.¹⁰⁵⁾

It has been proposed that the steady-state deformation above T_{po} would be resulted by the viscous flow occurring when the rate of Kear-Wilsdorf locking counterbalances with that of unlocking by atomic rearrangement by local short range diffusion.³⁶⁾ Thus, it is certain that the prerequisites for the occurrence of Johnston-Gilman-type yield drop is fulfilled,³⁶⁾ which are the low density of mobile dislocations before straining, the rapid dislocation multiplication and non-sensitivity on dislocation velocity to the stress.

No data are found on the stress at steady-state, τ_{oct}^* , as stated above. In order to visualize the effect of ternary elements on the plastic flow behaviour in the regime III, a temperature at which the 0.2% flow stress becomes to be 200 MPa, $T_{200 \text{ MPa}}$, is here defined.^{34,106)} Then the effect can be shown as Fig. 14, by which the additions of ternary elements raising $T_{200 \text{ MPa}}$ steeply are judged to be favourable for higher resistance against softening in the temperature regime.¹⁰⁶⁾ In these figures, the data presented by Curwick³⁰⁾ and Heredia^{31,32)} are used because there is no other systematic work done at a constant strain-rate. It is clear that the parameters such as E and K_0 in Eq. (14) should be strongly dependent on composition. It can be seen that the high temperature

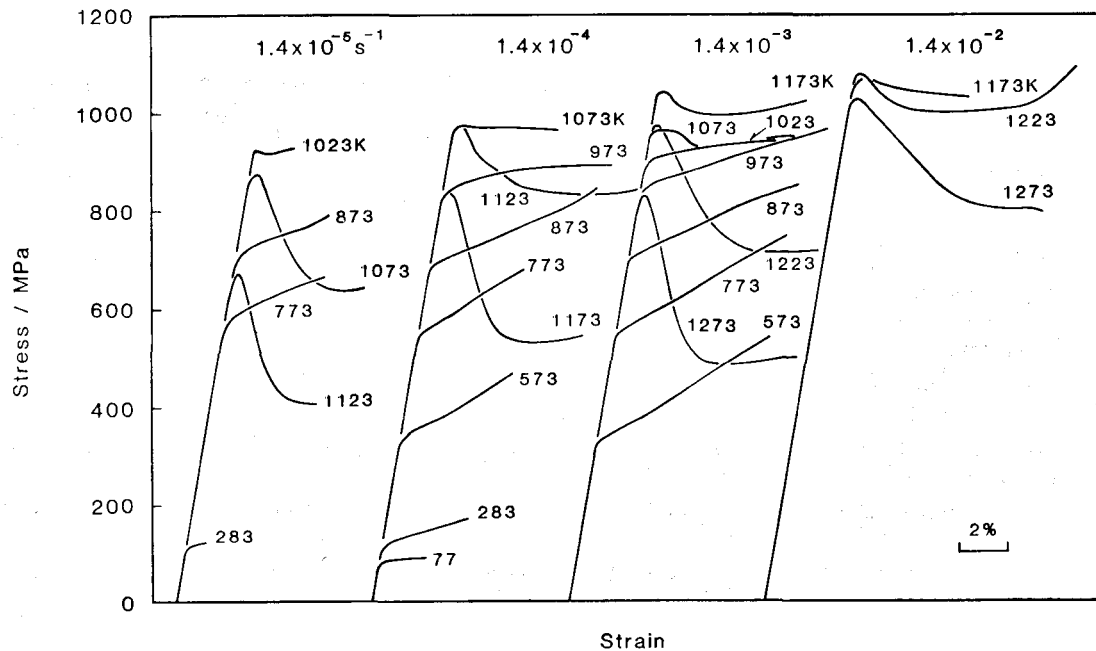


Fig. 13. Compressive stress-strain curves of $\text{Ni}_3(\text{Al}, \text{Ti})$ single crystals with an orientation near $[001]$ deformed at various temperatures at several strain-rates,³⁰⁾ showing the yield drop followed by steady state deformation.

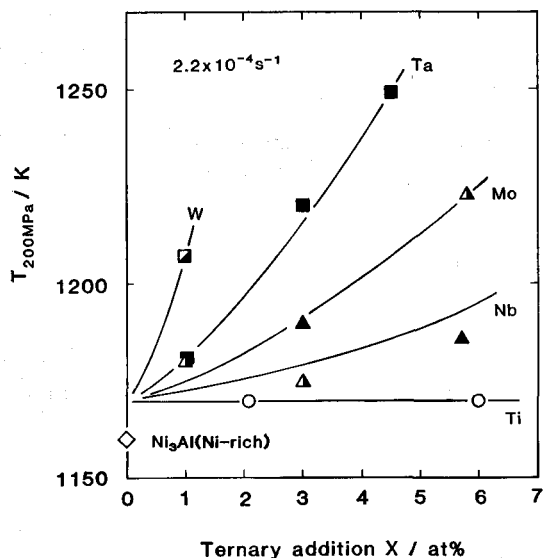


Fig. 14(a). Effect of ternary additions on the temperature at which the flow stress becomes 200 MPa, $T_{200 \text{ MPa}}$, which is defined as a measure for the high temperature strength,¹⁰⁶⁾ using the data obtained by Curwick at a constant strain-rate.³⁰⁾

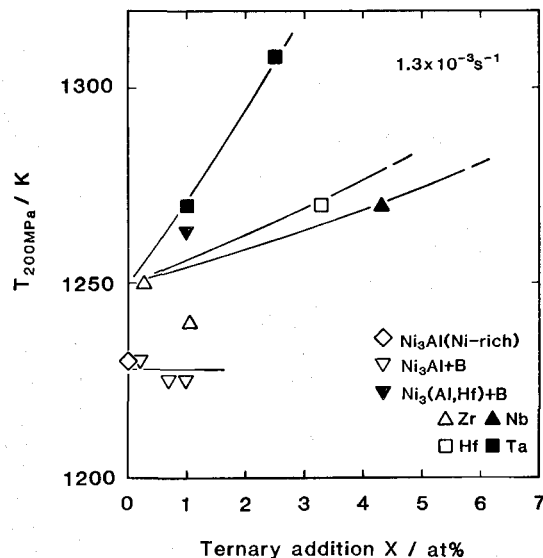


Fig. 14(b). Effect of ternary additions on the temperature at which the flow stress becomes 200 MPa, $T_{200 \text{ MPa}}$, which is defined as a measure for the high temperature strength,¹⁰⁶⁾ using the data obtained by Heredia at a constant strain-rate.^{31,32)}

resistance for the plastic flow is increased by an order of W, Ta, Mo, Nb and Ti in Fig. 14(a) and by an order of Ta > Hf > Nb > Zr in Fig. 14(b), presenting a good correlation with an order in the melting point of these elements. It then seems that self diffusion of the ternary element would control the magnitude of $T_{200 \text{ MPa}}$ and hence τ_{oct}^* .¹⁰⁶⁾

Although having been ignored until the work at high temperatures by Miura *et al.*,¹⁰⁶⁾ it should be noted that for orientations away from $[001]$ there are many experimental indications on the occurrence of a transition from cube slip to viscous octahedral slip, *i.e.*, from the regime II to the regime III, with fur-

ther increase in temperature.³⁴⁾ It can be often seen that some data for higher temperatures do not fit to the plot between the CRSS onto $(001)[110]$, τ_{cub} , and temperature T .³⁴⁾ It would be likely to happen if one sees the stronger negative temperature dependence of τ_{oct}^* than that of τ_{cub} in Fig. 1, where the transition temperature is denoted as T_t . Slip system controlling the creep deformation has not been reported. It is, however, speculated that the operative slip system at very slow strain-rate such as a creep condition would be octahedral viscous flow but not cube slip, irrespective of orientations of stress axis.

7. $L1_2$ Single Crystals Other than Nickel Base Compounds

7.1. Pt_3Al

Mention should be made on the plastic behaviour in single crystals of Pt_3Al reported by Wee *et al.*¹⁰⁷ and of Co_3Ti reported by Takasugi *et al.*¹⁰⁸

Pt_3Al exhibits another type of mechanical anomaly being different from what has been discussed here typically for Ni_3Al . A dramatic increase of the flow stress with decreasing temperature similar to that commonly observed in bcc metals has been reported in platinum base $L1_2$ compounds.^{18,20} Moreover, it has been observed in a single crystalline experiment that cube slip system dominates even at low temperatures unlike other fcc related compounds, with an exception where the stress axis is away from $[\bar{1}11]$ orientation.¹⁰⁷ It is interesting to note that the temperature dependence of plastic flow by cube glide of Pt_3Al is quite similar to that of Ni_3Al in the regime II. It is obvious that the temperature regime, where cube slip governs (the regime II), is moved down lower as a result of the competition for the choice of the operative slip systems.

This trend has been interpreted by Pope's group in terms of spreading core structure of superpartials into other planes to make them sessile.¹⁴ Yamaguchi *et al.*^{70,71} and Paider *et al.*⁷² have calculated the stability of dislocation structure in a model $L1_2$ lattice having different APB energies. They have concluded that in case of high APB and very low SF energies on (111) plane superdislocations should be separated by an SISF, because of unstable APB, and thus the core of these dislocations are extended spatially. Also, non-planar core structure should occur on (010) planes separated by an APB. They have expected that those sessile dislocations result in the high CRSS both on cube and octahedral planes at low temperatures in Pt_3Al .^{109,110}

Moreover, the group of the present authors has proposed that the substantial increase in flow stress at low temperatures is characteristic of such compounds that lie at phase stability boundary between $L1_2$ and U_3Si -type DO_c phase.^{28,111,112} It is interesting to note that Pt_3Al and Pt_3Ga have two polymorphisms being U_3Si -type phases, other than $L1_2$ phase.^{112,113} On the other hand, Pt_3Si and Pt_3Ge being U_3Si -type have no $L1_2$ phase.^{111,112} An attempt is underway to provide analytical description on such phase stability between the two phases in various alloy systems in terms of electron atom ratio as well as atomic radius ratio,¹¹⁴ for which the estimation of SF and APB energies in each phase becomes crucial.

7.2. Co_3Ti

The positive temperature dependence of strength in Co_3Ti has been reported first by Thornton *et al.*⁴ and later confirmed by Wee *et al.*¹⁸ in polycrystals. Single crystals of Co_3Ti containing 21~22 at% Ti¹⁰⁸ and of $(Co, Ni)_3Ti$ containing 3 at% Ni and 23 at% Ti¹¹⁵ have been examined by Izumi's group. The addition of 3 at% Ni is done in favour of single crystal growth, and it has been confirmed that Ni substitutes

for Co-site in Co_3Ti .¹¹⁶ In contrast to Pt_3Al , in Co_3Ti single crystals the plastic flow controlled by cube slip takes place at relatively higher temperatures. Takasugi *et al.*¹⁰⁸ have suggested that the decrease of the CRSS above T_{po} is probably due to the onset of diffusive process on (111) dislocation motion. This suggestion is easily acceptable because of the high value of T_{po}/T_m in Co_3Ti , where T_m is a melting point. The peak temperature T_{po} , where the onset of diffusive octahedral slip takes place, is estimated to be 0.6~0.77 T_m for Co_3Ti and $(Co, Ni)_3Ti$. In $Ni_3(Al, X)$, Ni_3Ga or Ni_3Ge single crystals having the stress axis close to $[001]$, T_{po} appears at 0.5~0.6 T_m .¹⁰⁸ It can be stated that the regime III in Co_3Ti exists at relatively high temperatures and the regime II controlled by cube slip takes place at higher temperature in Co_3Ti than in other nickel base $L1_2$ compounds. Also, T_{200MPa} has been estimated to be 1170 to 1180 K for both Co_3Ti and $(Co, Ni)_3Ti$ at a strain rate of 3.8 to $2.3 \times 10^{-3} s^{-1}$.¹⁰⁶ The peak temperature shift will be discussed again in Chap. 8.

It is observed in Co_3Ti that the CRSS for cube slip decrease sharply with increasing temperature and thus no distinct athermal stress $\tau_{G(ub)}$ can be estimated. At the same time it is reported that the CRSS is almost strain-rate independent and non-crystallographic slip trace is observed in the regime II beside cube slip trace.¹⁰⁸ Considering the above facts, it is suggested that the plastic behaviour of Co_3Ti at high temperatures is not the same as that of other nickel base $L1_2$ compounds and is not controlled by such single mechanism that is mentioned in Chap. 6, because the regime II is shifted toward relatively high temperature as compared to its melting point. It is concluded that the dominancy for (111) slip over (001) slip in Co_3Ti at elevated temperatures is not responsible for the ease of diffusive (111) slip but rather for the difficulty in operating (001) slip as a result of very high T_c for τ_{cub} .

7.3. Low Temperature Sensitivity of Flow Stress

Below room temperature, Pt_3Al and Co_3Ti show the rapid increase of the flow stress with decreasing temperature, as stated above. It is true that the CRSS for both octahedral and cube slip in Pt_3Al and the CRSS for octahedral slip in Co_3Ti are controlled by a thermally activated process, which overcomes an innate lattice resistance to dislocation motion or the Peierls stress. If a single mechanism is rate-controlling, it is convenient to introduce the third stress component τ'_{oct} to Eq. (1), which might depend sensitively on temperature T and strain-rate.

$$\tau_{oct} = \tau_{G(oct)} + \tau'_{oct}(T, \dot{\gamma}) + \tau'_{oct} \dots \dots \dots (15)$$

The function of $\tau'_{oct}(T, \dot{\gamma})$ is not known at present but might be similar to that of τ_{cub} .

In Co_3Ti at low temperatures $\tau'_{oct}(T, \dot{\gamma})$ is the larger component, while at higher temperatures τ'_{oct} is the larger component.¹⁰⁸ Annealing twins have been frequently observed in a deformed Co_3Ti in the study on recrystallization¹¹⁷ and a very low phase stability of Co_3Ti against DO_{24} phase, which consists of a mix-

ture of cubic and hexagonal stackings, has been confirmed in a study on the pseudobinary $\text{Co}_3\text{Ti-Ni}_3\text{Ti}$ phase diagram.¹¹⁸⁾ These facts strongly suggest that Co_3Ti has very low SF energy which reconciles itself to the theory of non-planar dislocation core structure.^{109,110)} In $(\text{Co, Ni})_3\text{Ti}$, it has been shown by TEM *in situ* observation that the SISF type dissociated pairs being sessile converts into the APB type dissociated pairs being glissile under an applied stress and the core transition is reversible.¹¹⁹⁾ This is likely to be one of the experimental evidences in favor of the core structure mechanism proposed.

Evidence contrary to this idea is that no twin has been observed in as cast Pt_3Al nor Pt_3Ga .¹¹²⁾ Similar low temperature sensitivity of flow stress has been observed in Ni_3Mn ¹²⁰⁾ and Cu_3Pt ¹²¹⁾ being Kurnakov compounds. It is felt that further works are necessary to answer the question whether the thermal component of the stress $\tau_{\text{oct}}^L(T, \dot{\gamma})$ in these $L1_2$ compounds including Pt_3Al and Co_3Ti is controlled by the same mechanism.

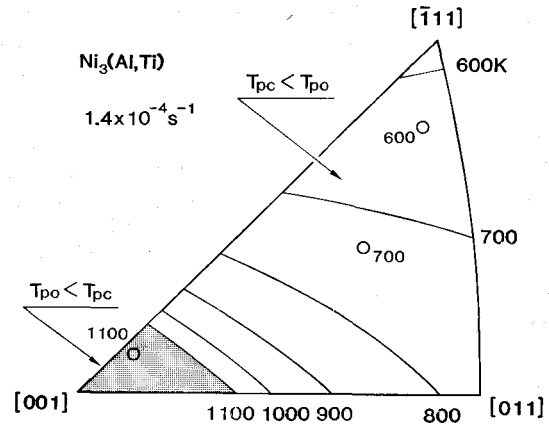
8. Peak Temperatures

It then becomes possible to provide a criterion for the appearance of particular peak temperatures in $\text{Ni}_3(\text{Al, Ti})$, T_{pc} or T_{po} , depending on the crystallographic orientations by considering relative magnitude of the RSS on relevant planes.³⁶⁾ The condition, under which octahedral slip governs the plastic deformation in regime III, is that the RSS for $(111)[\bar{1}01]$, $R\tau_{\text{oct}}$, exceeds τ_{oct}^* before that for $(001)[\bar{1}10]$, $R\tau_{\text{cub}}$, does τ_{cub} . It is expressed as;

$$R\tau_{\text{oct}}^* < R\tau_{\text{oct}} < \tau_{\text{cub}}. \dots\dots\dots(16)$$

Fig. 1 depicts two situations where the condition holds or not depending on the orientation of the single crystals. For the orientation A being away from $[001]$, the value of R is larger than the unity and consequently the inequality (16) is not satisfied. Then the relative magnitude of relevant shear stresses as a function of temperature is as Fig. 1. For the orientation B being near $[001]$ where the value of R is much smaller than the unity, the situation is as shown in Fig. 1 and T_{po} becomes visible. The choice of slip system for different orientations of stress axis mostly depends upon the geometrical restrictions. For stress axes located on the $[001]$ side of the unit triangle, octahedral slip tends to occur, whereas for those on the other side, cube slip is preferred.

The above argument on the orientation dependence of the peak temperature can be extended to be more quantitative by taking the shear strain-rate dependence of stresses into account to examine the validity of the inequality (16). Using the state equations derived so far in the text, the condition under which $T_{po} < T_{pc}$ can be analytically obtained.³⁶⁾ We can define here that T_{po} is the temperature at which τ_{oct} is equal to τ_{oct}^* . These conditions can be expressed using Eqs. (1), (3) and (14) with proper assignments on the constant values. The result for $\text{Ni}_3(\text{Al, Ti})$ at a constant strain-rate is shown in Fig. 15, where T_{pc} contours are drawn and the region in



Circles are the orientations examined.
Numerals are observed T_{pc} and T_{po} .
The region where $T_{po} < T_{pc}$ holds is hatched.

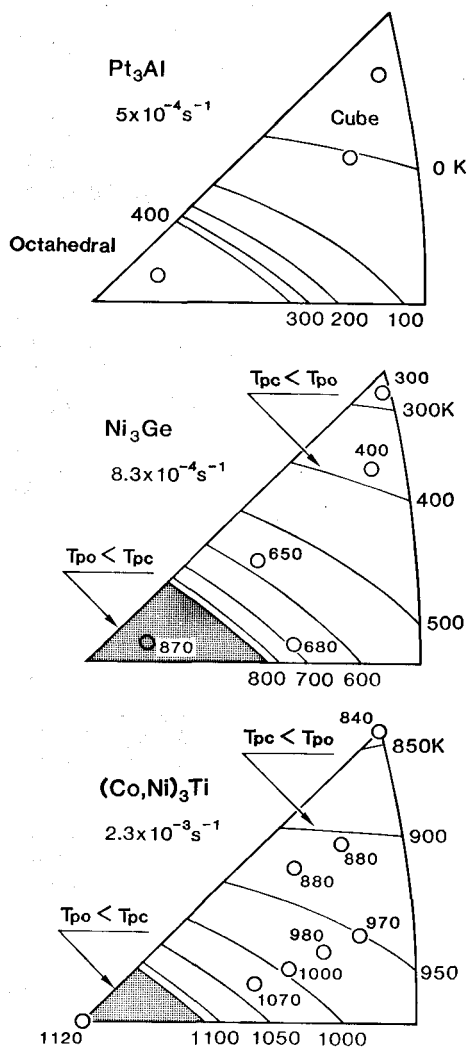
Fig. 15. T_{pc} contour in the unit triangle at a constant strain rate of $1.4 \times 10^{-4} \text{ s}^{-1}$ for $\text{Ni}_3(\text{Al, Ti})$ single crystal.³⁶⁾

which $T_{po} < T_{pc}$ holds is hatched.³⁶⁾ As a result, a transition boundary exists between two area in the unit triangle which location depends on controlling mechanism of the slip systems being temperature and more or less strain-rate sensitive.^{36,110)} Note that the transition boundary between the slip systems is governed by R -value and the strain-rate as is indicated in Eqs. (12) and (14). Nevertheless, the boundary and the contour of T_{pc} are mostly located along equi-values of R . (see Appendix)

The peak temperature T_{pc} is determined by the condition of $R\tau_{\text{oct}} = \tau_{\text{cub}}$. The peak shift to lower temperature is likely to occur in $\text{Ni}_3(\text{Al, X})$ single crystals by the additions of ternary element, within a limited number of systematic observations.^{36,122)} This feature can be easily explained by the following two facts. In most cases for the sake of the increase of the solid solution hardening and the decrease of the activation energy U by the ternary additions the rapid increase of τ_{oct} occurs with increasing temperature, as shown in Fig. 7. On the other hand, although the effect of the ternary additions on τ_{cub} has not fully known yet, there is no considerable effect on τ_{cub} , one of the components of τ_{cub} , as shown in Fig. 12. Similar observation has been done on the work for $(\text{Co, Ni})_3\text{Ti}$ single crystals examined by Izumi's group.¹¹⁵⁾ It is obvious that the addition of Ni reduces the peak temperature of Co_3Ti , because of the rapid increase in τ_{oct} with increasing temperature. The fact that the partial substitution of Ni enhances the mechanical anomaly of Co_3Ti is also in accord with the phase stability concept concerning to the electron atom ratio. In contrast to the above, it has been reported by Pak *et al.*⁷⁹⁾ that the small addition of Co in Ni_3Ge does not markedly affect τ_{oct} but does τ_{cub} and the critical temperature T_c are reduced. Thus, the peak shift occurs to lower temperatures in $(\text{Ni, Co})_3\text{Ge}$,⁷⁸⁾ contrary to $(\text{Co, Ni})_3\text{Ti}$. In various kinds of $L1_2$ compounds, the comparison of T_{pc} can be made at similar orientations close to $[\bar{1}11]$ and at similar strain-rates of $10^{-3} \sim 10^{-4}$ as follows; at 650 K for $\text{Ni}_3(\text{Al, Nb})$,⁹¹⁾ at 600 K for $\text{Ni}_3(\text{Al, Ti})$,³⁵⁾ at 720

K for Ni_3Ga ,¹²³⁾ at 300 K for Ni_3Ge ⁷⁷⁾ and at 900 K for Co_3Ti .¹⁰⁸⁾ Among these $L1_2$ compounds, it has been reported that T_e is inversely related to $\tau_{G(\text{cub})}$ and proportionally related to T_{pc} .⁹⁹⁾

Single crystal superalloys with the orientation near [001] have superior high temperature capability, because of the occurrence of the highest peak temperature among all other orientations. It is therefore practically important to know how the ternary additions affect the peak temperature T_{po} in $\text{Ni}_3(\text{Al}, X)$ single crystals. In Chap. 6, it is demonstrated that the substitution of refractory transition metals increases the parameter $T_{200 \text{ MPa}}$ and hence τ_{oct}^* . The increase of τ_{oct} caused by the Kear-Wilsdorf locking with increasing temperature will continue until the condition of $\tau_{\text{oct}} = \tau_{\text{oct}}^*$ is attained. It is concluded that the substitution of refractory metals, which reduce the diffusion rate, raises T_{po} in $\text{Ni}_3(\text{Al}, X)$ single crystals having the orientation near [001]. This feature can be really seen on the data obtained by Curwick.⁸⁰⁾ The comparison on T_{po} can be made at similar orientations close to [001] and at similar



Circles are the orientations examined. Numerals are observed T_{pc} and T_{po} . The region where $T_{po} < T_{pc}$ holds is hatched.

Fig. 16. T_{pc} contour in the unit triangle for Pt_3Al , Ni_3Ge , and $(\text{Co}, \text{Ni})_3\text{Ti}$ single crystals.¹²⁴⁾

strain-rates as follows; at 1 100 K for $\text{Ni}_3(\text{Al}, \text{W})$,⁸⁶⁾ at 1 150 K for $\text{Ni}_3(\text{Al}, \text{Ti})$,⁸⁶⁾ at 920 K for Ni_3Ga ,⁶⁾ at 870 K for Ni_3Ge ⁷⁷⁾ and at 1 130 K for Co_3Ti ¹⁰⁸⁾ and $(\text{Co}, \text{Ni})_3\text{Ti}$.¹¹⁵⁾ In all compounds, T_{po} is well above $0.5T_m$, where the diffusion controlled process might begin. It is interesting to note that T_{po} is extended to higher temperatures being well above $0.6T_m$ even in Ni_3Ge , which have a very low T_{pc} , compared to other $L1_2$ compounds,⁷⁷⁾ as stated above.

Based on the experimentally obtained data for the temperature dependence of the CRSS for both (111) $[\bar{1}01]$ and (001) $[\bar{1}10]$ slips, it is possible to estimate the transition boundary in the unit triangle on each $L1_2$ compound. This has been done in Figs. 16 and 17 for Pt_3Al , Ni_3Ge , and $(\text{Co}, \text{Ni})_3\text{Ti}$,¹²⁴⁾ taking into account the N -dependence of the strength anomaly. The calculated transition temperatures of T_{po} and T_{pc} are summarized at a constant strain-rate on the unit triangle in Fig. 16 and as a function of R -value in Fig. 17. From these figures together with Fig. 15, it can be seen the different characters in the transition behaviour from octahedral to cube slip systems in several kinds of $L1_2$ compounds. It is found in general, T_{pc} increases first gradually and then steeply with decreasing R -value. By the truncation upon the onset of viscous flow on octahedral plane, being independent on the R -value, T_{po} takes place at region of smaller value of R . As a deformation map, the transition temperature from cube slip to viscous octahedral slip, being termed as T_t , can be drawn to form a triple point, as indicated in Fig. 17.

To be noted is that the temperature regime between T_{po} and T_t , *i.e.*, the regime II, is found much narrower for $(\text{Co}, \text{Ni})_3\text{Ti}$ than for other $L1_2$ compounds. This situation would make difficult to experimentally visualize transition of the slip systems, as evidenced by the result obtained by Takasugi *et al.*¹⁰⁸⁾ The result for Pt_3Al is somewhat different

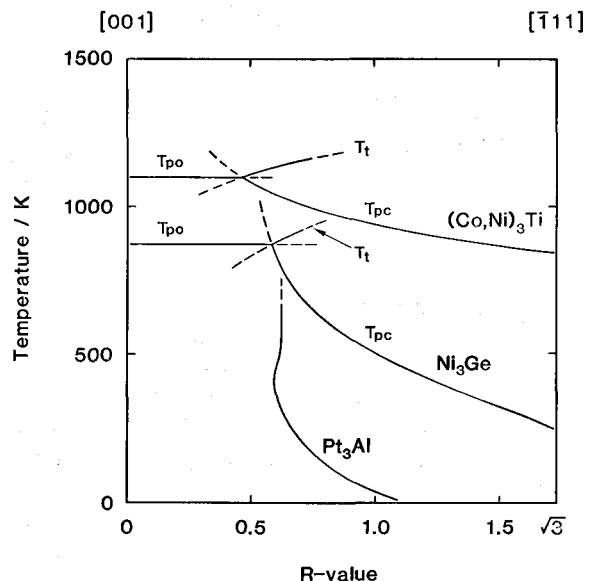


Fig. 17. Orientation dependence, R -dependence (see Appendix), of the transition temperatures, T_{pc} , T_{po} and T_t , in Ni_3Ge , Pt_3Al and $(\text{Co}, \text{Ni})_3\text{Ti}$ single crystals.¹²⁴⁾

where a slight retrogression on the R -dependence of T_{pc} is observed. However, it is not conclusive because the high temperature plastic behaviour is not taken into account in this calculation. It is evident that additional works are needed on the plastic behaviour of these compounds including Pt_3Al in terms of the strain-rate sensitivity, the temperature dependence of flow stress at high temperatures and the behaviour of dislocations.

Note that the occurrence of the peak of flow stress in polycrystals is rather complicated. It would be caused not only by the onset of cube slip or viscous octahedral slip but also by grain boundary sliding or cracking, the latter being dependent on the grain size and the nature of grain boundary.¹²⁵⁻¹²⁷⁾

9. Future Scope

This review demonstrates that the plastic behaviour in $Ni_3(Al, X)$ single crystals are clearly understood in terms of the dependent variables, *i.e.*, temperature, strain-rate, orientation and compositions including the deviation from stoichiometry and the ternary additions. As a summary, the list of the experimental works on the mechanical properties of $L1_2$ single crystals, mostly related to the temperature dependence of flow stress, is shown in Table 1.

The above situation will stimulate us to establish the mathematical modeling for the estimation of flow stress in $Ni_3(Al, X)$ single crystals. It can predict, for example, the limit of mechanical properties of gamma prime such as the peak strength and the peak temperature within the maximum solid solubility of ternary elements. Toward further development of superalloys being more useful, this program could be extended to nickel base alloys with high volume of γ' , especially unidirectionally solidified alloys. In the γ/γ' two phase alloys, the additional effects on the strength must be taken into account,^{14,144)} the volume fraction and the size of γ' , the misfit between γ and γ' and the APB energy of γ' . Clear relations describing those effects, theoretical or empirical, have not been fully understood yet and enough data supporting them is still lacking. The establishment of reliable Ni-Al-X phase diagrams is claimed. Especially, the partitions of solute elements into γ and γ' , *i.e.*, the equilibrium compositions of γ and γ' , must be established.

No-man's-land still remains widely in the $L1_2$ single crystal world. Concerning to the mechanical behaviour of Ni_3Al single crystals, the works on $Ni_3-(Al, X)$, $(Ni, X)_2Al$ and $(Ni, X)_3(Al, X)$, are needed, where X stands for B-subgroup elements substituting mostly for Al-site, for transition metals such as Co, Cu or Pt substituting mostly for Ni-site and for transition metals such as Fe or Cr substituting for both sites, respectively. Investigations on the $Ni_3(Al, X)$ single crystals containing B-subgroup elements provide us with the comprehensive understanding on the relation between the plastic behaviour and the phase stability of $L1_2$ phase, although they might have no practical importance. The addition of Cr is of importance for the improvement of oxidation resistance of γ' single crystals.

The experimental works on quaternary Ni_3Al are also inevitable in order to check the additivity of the respective effects of a solute element and a second solute element. Among these, special attention should be paid to the pseudobinary Co_3Ti-Ni_3Al system, where the continuous solid solution of $L1_2$ phase is formed.²⁷⁾ The compounds being close to Co_3Ti -side might be candidates for the practical application for high temperature use, because we could combine both the characters; *i.e.*, good ductility and low diffusivity in Co_3Ti and the high stability for compositional modifications in Ni_3Al . The effect of ternary elements needs to be investigated on APB and SF energies theoretically and experimentally, by means of electron microscope¹⁴⁵⁻¹⁴⁷⁾ or FIM,^{148,149)} in order to confirm further the relevance of the phase stability with the characteristic mechanical properties and the dislocation configurations.

The ternary elements such as carbon and boron, being interstitially soluble, would markedly affect the mechanical properties. The experiments on the effect of B addition in single crystals is underway in Pope's laboratory.³²⁾ Beside the improvement of ductility of polycrystals, the role of B is found to increase the low temperature strength $\sigma_{0(oct)}$ or $\tau_{0(oct)}$,^{32,55)} and the mechanical anomaly.^{32,85)} However it does not affect the high temperature characteristics such as $\tau_{G(cub)}$ and $T_{200 MPa}$ as can be seen in Figs. 12 and 14(b).^{32,106)}

The experiments on other $L1_2$ single crystals to be done can be suggested. Among 4 Ni base $L1_2$ compounds, only Ni_3Si single crystals have not been treated yet. Polymorphisms of Ni_3Si ¹⁵⁰⁾ prevent the growth of single crystals by Bridgman method. It's possibility would become large, for example, by the partial substitution of Ti, one of few elements being accommodated into Ni_3Si .⁹⁾ The works on Pt_3Al and Co_3Ti single crystals are of significance as is mentioned in the previous chapter. The temperature dependence of elastic constants of Ni_3Al by Ono and Stern⁶⁰⁾ and by others¹⁵¹⁻¹⁵³⁾ is of great value. The effect of ternary additions on the elastic constants of Ni_3Al has been reported in single crystals by Curwick³⁰⁾ and in polycrystals by Mishima *et al.*¹¹⁾ The data for elastic constants for other $L1_2$ single crystals are necessary. Recently, Yoo¹⁵⁴⁾ has pointed out that the driving force of the cross slip in $L1_2$ compounds is supplied by not only anisotropy of APB energy but also anisotropy of elasticity for screw component dissociated to APB or SISF.

Although there is every indication for theoretical¹⁵⁵⁾ and experimental works on work hardening^{66,88,98,129)} including latent hardening,^{128,156)} cyclic hardening¹⁵⁷⁻¹⁵⁹⁾ and fracture stress^{88,128)} and on fatigue,^{160,166)} much more works are needed in this field. Much progress has been made in deducing the mechanisms of plastic behaviour in Ni_3Al as described here and a lot of data has been compiled on the creep properties on the γ/γ' alloys.¹⁴⁾ It is rather surprising that there have been only a few investigations on the creep properties not only of single crystalline Ni_3Al ¹⁶¹⁻¹⁶³⁾ but also of polycrystalline Ni_3Al .^{2,102,164)} Our current knowledge is quite limited on the creep behaviour of

7	75	10	S	1.3E-3	T	—	102.0	—	—	1 125	6.4/4.8	[5]FR	79) Aoki ⁽⁸⁹⁾
8	75	10	S	1.3E-3	T	63.4	118.9	140	1 300	(1 255)	6.4/4.8	[1]	86) Chang ⁽¹⁰²⁾
9	75.0	5.0	N	1.4E-2	C	37.1	54.1	150	1 550	1 340	9.4	[3]	87) Miura ⁽⁹⁵⁾ & 87) Ochiai ⁽³⁰⁾
				1.4E-3	C	37.1	54.1	150	1 315	1 280	9.4		
				1.4E-4	C	37.1	54.1	150	1 140	1 190	9.4		
				1.4E-5	C	37.1	54.1	150	1 010	1 110	9.4		
10	75.1	6.1	N	3 E-4	C	—	99.5	130	1 150	—	8.9	[1]WH	83) Staton-B ⁽¹⁰⁰⁾
11	75.19	9.78	N	8.3E-4	T	51.8	96.5	125	1 200	—	6.8	[11]FR	88) Kim ^(83,136)
12	75.7	5.1	N	3 E-4	C	—	70.9	165	1 175	—	10.2	[1]	75) Staton-B ⁽⁹⁸⁾
13	76.0	5.3	N	3 E-4	C	—	62.8	—	—	—	10.5	[1]	75) Staton-B ⁽⁹⁸⁾
14	77.8	5.6	N	3 E-4	C	—	52.7	145	—	—	12.6	[1]	75) Staton-B ⁽⁹⁸⁾
15	77.85	7.35	N	2 E-4	C	141.8	143.0	—	—	—	11.5	[3~6]	76) Travina ⁽³⁾
Ni ₃ (Al, Ti)+B													
1	76.00	5.00	N	5.2E-4	T	—	135.8	—	—	—	10.7	[8]FR	88) Kim ⁽³⁴⁾
		+B											
		0.24											
2	76.00	5.03	N	8.3E-4	T	92.7	137.0	—	—	—	10.6	[3]FR	88) Kim ⁽³⁸⁾
		+B											
		0.23											
Ni ₃ (Al, V)													
1	75	5	S	8.3E-4	T	—	49.8	—	—	—	9.0/7.4	[7]FR	88) Kim ⁽³⁶⁾
Ni ₃ (Al, W)													
1	75	3	S	?	C	58.5	70.5	—	—	—	9.2/7.6	[1]*1	73) Mulford ⁽⁶⁰⁾
						59.6[$\tau_{occ(4)}$]							
2	75	3	S	2.6E-3	C	67.7	90.6	200	1 200	—	9.2/7.6	[1]*2	78) Kuramoto ⁽⁸⁷⁾
3	75.3	1.0	N	2.2E-4	C	—	51.3	120	1 400	1 210	11.2	[3]	72) Curwick ⁽³⁰⁾
4	75.7	2.9	N	8.3E-4	C	48.2	86.8	150	1 200	—	10.2	[6]	77) Saburi ⁽³⁷⁾
Ni ₃ (Al, Zr)													
1	76.09	0.26	N	1.3E-3	C, T	56.2	61.7	110	1 450	1 250	13.0	[5]	88) Heredia ⁽⁸²⁾
2	76.17	1.04	N	1.3E-3	C, T	94.8	94.9	120	1 450	1 250	11.2	[7]	88) Heredia ⁽⁸²⁾
Ni ₃ Ga													
1	74.3	—	A	1.1E-4	C	36.7	56.1	—	—	—	7.7	[2]	80) Pak ⁽²³⁾
2	74.6	—	A	1.2E-4	C	26.4	39.0	120	1 000	—	8.2	[3]	73) Takeuchi ⁽⁹⁾
3	74.8	—	A	1.3E-3	C, T	85.6	91.8	130	1 025	1 080	8.6	[6]	87) Ezz ⁽⁸²⁾
Ni ₃ Ge													
1	77.1	—	N	8.3E-4	C	92.4	190.9	260	800	—	6.3	[5]	75) Pak ⁽⁷⁷⁾
2	76.88	—	N	8.3E-4	T	—	153.4	—	—	—	6.0	[8]FR	88) Kim ⁽⁸⁶⁾
3	76.8	—	N	1.3E-3	T	139.0	180.4	—	—	—	5.9	[7]	78) Aoki ⁽²⁹⁾
4	76.8	—	N	1.3E-3	T	—	189.5	—	—	—	5.9	[7]	79) Aoki ⁽⁸⁰⁾
(Ni, Co) ₃ Ge													
1	75.2	1.5	N	8.3E-4	C	75.2	169.6	250	650	—	—	[1]	76) Pak ⁽⁷⁸⁾
2	76.2	0.6	N	8.3E-4	C	74.6	186.0	250	650	—	—	[4]	76) Pak ⁽⁷⁸⁾
Co													
X													
Co ₃ Ti													
1	78.0	—	N	3.8E-3	C	—	43.5	<145	1 400	1 180	—	[5]	87) Takasugi ⁽¹⁰⁸⁾
				3.8E-4	C	—	43.5	<145	1 400	1 175	—	—	—
2	78.5	—	N	3.8E-3	C	64.7	35.4	—	—	(1 250)	—	[5]	87) Takasugi ⁽¹⁰⁸⁾
				3.8E-4	C	64.7	35.4	—	—	(1 130)	—	—	—
3	78.99	—	N	3.8E-3	C	74.5	44.1	<140	(1 400)	(1 200)	—	[5]	87) Takasugi ⁽¹⁰⁸⁾
				3.8E-4	C	74.5	44.1	<140	(1 400)	(1 180)	—	—	—

(... to be continued)

Table 1. Continued.

Alloy system	No.	Composition (at%)		Strain-rate (s ⁻¹)	C/T	$\tau_{G(\text{oct})}$ (MPa)		$\tau_{G(\text{cub})}$ (MPa)	T_c (K)	T_{500} MPa (K)	U_{poly} (KJ·mol ⁻¹)	Remarks	Ref.	
		Co	X			$\tau_{\text{oct}(RT)}$	$\tau_{\text{oct}(RT)}$							
(Co, Ni) ₃ Ti	1	74	3	N	C	69.3	40.2	120	1 300	1 190	—	[8]	88) Liu ⁽¹⁸⁾	
						87.9	$[\tau_{\text{oct}(4)}]$							
Pt ₃ Al	1	73	—	N	5 E-4	692.0	553.0	310	450	—	—	[3]	84) Wee ⁽⁹⁷⁾	
						690.0	$[\tau_{\text{oct}(4)}]$	341.5	$[\tau_{\text{cub}(RT)}]$					
								619.0	$[\tau_{\text{cub}(77)}]$					
								760.0	$[\tau_{\text{cub}(4)}]$					
Cu ₃ Au	1	75	—	S	1.2E-4	15.6	14.1	—	—	—	—	[1]	72) Pope ⁽⁸²⁾	
	2	75	—	S	1.2E-4	16.5	16.9	—	—	—	—	[1]	73) Pope ⁽⁸³⁾	
	3	75	—	S	9.5E-4	15.3	17.3	$[\tau_{\text{oct}(4)}]$	—	—	—	[4]*	76) Kuramoto ⁽⁸²⁾	
	4	75	—	S	9.5E-5	15.3	15.6	—	—	—	—	[4]WH*	76) Kuramoto ⁽⁸⁴⁾	
	5	75	—	S	1.0E-3	16.6	16.2	—	—	—	—	[2]WH	65) Davics ⁽⁸⁶⁾	
	6	75	—	S	3.3E-4	—	16.1	—	—	—	—	[1]WH	75) Sastry ⁽⁸⁷⁾	
	7	75	—	S	1 E-3	—	13.2	—	—	—	—	[3]WH	64) Kear ⁽⁸⁸⁾	
Cu ₃ Pt	1	77.0	—	N	1.4E-4	44.9	37.4	—	—	—	—	[3]	88) Miura ⁽²¹⁾	
	2	81.0	—	N	1.4E-4	38.5	24.6	—	—	—	—	[3]	88) Miura ⁽²¹⁾	
	3	85.0	—	N	1.4E-4	43.8	30.2	—	—	—	—	[3]	88) Miura ⁽²¹⁾	
Cu ₃ Pt+In	1	77.0+In	1.0	N	1.4E-4	43.6	29.6	—	—	—	—	[2]	88) Miura ⁽²¹⁾	
Ni ₃ Fe	1	75	—	S	5.2E-4	49.9	38.8	—	—	—	—	[8]FR	88) Kim ⁽⁸⁶⁾	
	2	73.87	—	A	1.0E-4	36.3	30.8	—	—	—	—	[2]	81) Wee ⁽⁸¹⁾	
	3	72.1	—	A	1.0E-4	69.8	60.9	—	—	—	—	[11]WH	68) Victoria ⁽⁸⁵⁾	
Ni ₃ Mn	1	75?	—	?	?	107.1	81.7	—	—	—	—	[5~6]WH	73) Nosova ⁽²⁹⁾	

Ref. & Fig.
[Fig. in the text]

A: Minority component-rich side
S: Stoichiometry
N: Majority component-rich side

C: Compression test
T: Tension test
(): Uncertainty

[]: Number of orientations examined
*1 0.1% flow stress
*2 Same batch as above

WH: Work hardening
FR: Fracture behaviour
LH: Latent hardening

$\text{Ni}_3(\text{Al}, X)$ single crystals. It is urgently needed to investigate the slip system operating during creep and the composition and orientation dependences of the creep rate and to construct the deformation mechanism map for Ni_3Al . Data for inter-diffusion in $L1_2$ compounds are also necessary.

Acknowledgements

The authors express their appreciation to Prof. D. P. Pope and Dr. F. E. Heredia of University of Pennsylvania for providing a lot of data invaluable for $\text{Ni}_3(\text{Al}, X)$ and $\text{Ni}_3\text{Al}+\text{B}$ single crystals. Thanks are also due to Profs. O. Izumi, S. Hanada and Dr. Takasugi of Tohoku University for providing manuscripts related to $(\text{Co}, \text{Ni})_3\text{Ti}$ single crystals.

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Note: The results of $\text{Ni}_3\text{Al}+\text{B}$ single crystals referred in the text have been presented by Heredia and Pope of University of Pennsylvania in 1988 Fall Meeting of MRS held in Boston. Details will be appeared in the proceedings "High Temperature Ordered Intermetallic Alloys III". $\text{Ni}_3(\text{Si}, \text{Ti})$ containing 11 at% Si and 11 at% Ti has been presented by Kim, Hanada and Izumi in 1988 Fall Meeting of Japan Inst. Met. held in Osaka.

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Appendix

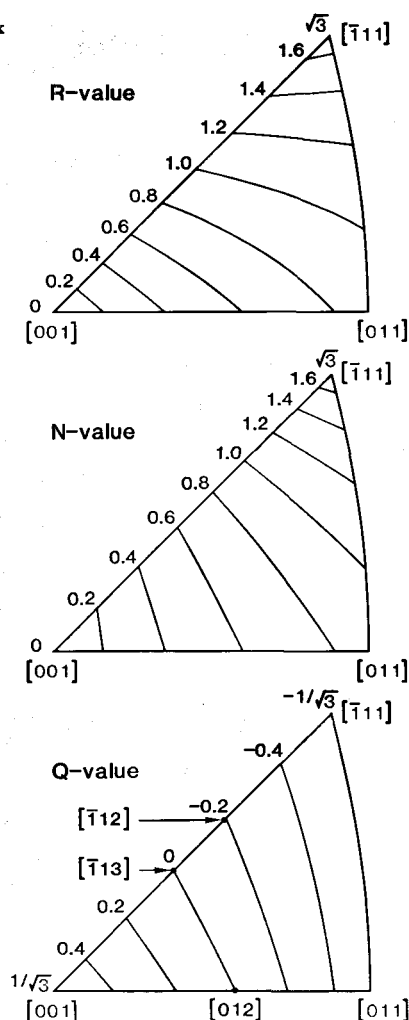


Fig. A-1. Plots of various Schmid factor ratios, R -, N - and Q -values on the unit triangle.

$$R = \frac{S_c}{S_o} = \frac{\text{Schmid factor on } (001)[\bar{1}10]}{\text{Schmid factor on } (111)[\bar{1}01]}$$

$$N = \frac{S_n}{S_o} = \frac{\text{Schmid factor on } (010)[\bar{1}01]}{\text{Schmid factor on } (111)[\bar{1}01]}$$

$$Q = \frac{S_q}{S_o} = \frac{\text{Schmid factor on } (111)[\bar{1}2\bar{1}]}{\text{Schmid factor on } (111)[\bar{1}01]}$$

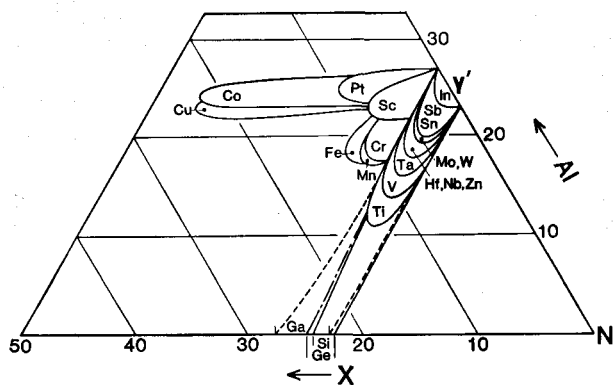


Fig. A-2. Semischematic depiction of the solubility lobes of ternary Ni_3Al phase with various solutes mostly at 1273 K.^{9,10)}