Ab-Initio Lattice Instability Analysis on Ni and Ni₃Al Single Crystals*

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The purpose of the present study is to elucidate the “ideal strength” of the Ni and Ni₃Al single crystals, the main compositions of Ni-based superalloy, from the viewpoint of the lattice stability. The unit lattices of Ni and Ni₃Al, fcc and L1₂ ordered alloy, are subjected to the [001] uniaxial tension/compression and hydrostatic tension/compression by using the Vienna Ab-initio Simulation Package (VASP) with the generalized gradient approximation (GGA) and ultrasoft pseudopotential. The elastic stiffness matrix is numerically evaluated at each point in the applied deformation pass, then the lattice stability is discussed based on the positiveness of the matrix. Both Ni and Ni₃Al reach the Born’s stability criteria against the bifurcation to the anisotropic Poisson’s contraction in the [001] uniaxial tension, while they do the spinodal criteria against the structural transformation in the [001] uniaxial compression and hydrostatic tension. The hydrostatic compression increases the stability and shows no limit, however, it is also suggested that the spinodal instability appears when the ideal isotropy was broken. The “ideal strength” is evaluated with these stability limits and indicated as “yield curve” on the normal strain-lateral strain or normal stress-lateral stress planes.

Key Words: Lattice Instability, Ab-Initio Simulation, Bifurcation, Ni-Based Superalloy

1. Introduction

Ab-initio calculations based on the density functional theory (DFT) have drawn keen interest as a potential method in material designing; since it can precisely predict the material properties from the electronic state and expel the conventional trial-and-error experiment. The method, however, can so far treat too small amount of atoms to simulate deformation behavior in the enormous degree of freedom, e.g. dislocation nucleation and motion. Thus some DFT studies discuss the strength and worka-

bility of materials by the ideal shear strength in the slip direction⁽¹⁾ or the stacking fault energy for the dislocation mobility⁽²⁾. The mechanism of deformation and fracture, however, varies case by case depending on the local mechanical conditions such as hydrostatic stress generated by deformation constraint. For more precise prediction of the strength of real materials, the DFT studies should consider not only the maximum strength in the assumed deformation pass but also the elastic limit against various deformation modes.

The lattice instability analysis^{(3)–(5)} has long devoted to the energetics of ideal crystals, of which deformation is represented by a Bravais lattice, for the theoretical strength of “continuum”. The DFT calculation is well-suited to the lattice instability analysis since it cannot treat a large number of atoms but evaluate the system energy exactly even in the large deformation where the classical interatomic potential functions lose the transferability. Thus we have implemented the “ab-initio lattice instability analysis”, or the lattice instability analysis by the *ab-initio* molecular dynamics (statics) simulation, for the first principle prediction of material strengths⁽⁶⁾. In the present study, the unit lattices of Ni and Ni₃Al, the main compositions of Ni-based superalloys, are subjected

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to the [001] uniaxial tension/compression and hydrostatic tension/compression by means of the *ab-initio* molecular statics simulation. Then the elastic limit of the lattices are discussed from the viewpoint of the lattice stability to obtain the “yield curve” against the various deformation modes, anticipating the first principle insight on the strength of the γ/γ' interfaces in Ni-based superalloys.

2. Instability Criteria Based on Elastic Stiffness Coefficients

In the earlier studies of the lattice instability analysis^{(4),(5)}, the second order derivatives of the energy function is strictly derived in the definite mathematical form for the ideal homogeneous lattice represented by a Bravais lattice. On the other hand, Wang et al.⁽⁷⁾ proposed the stability criteria based on the positiveness of the elastic stiffness coefficients⁽⁸⁾, which are numerically evaluated in the atomic simulations. That is, the affine deformation with the six strain parameters is assumed on the crystals while they actually have the internal inhomogeneity such as thermal vibration or lattice defects. The Wang's criteria is applicable to the DFT calculation even though the strict mathematical equation of the second order derivatives could not be given in the DFT.

Assume a crystal is in the equilibrium under external load at the current configuration $\mathbf{X}$. The stress at the other configuration $\mathbf{x}$, which is slightly deformed from $\mathbf{X}$, is given by the following Taylor series expansion against small strain perturbation:

$$\sigma_{ij}(\mathbf{x}) = \sigma_{ij}(\mathbf{X}) + B_{ijkl}(\mathbf{X})\Delta\eta_{kl} + \cdots \quad (1)$$

Here

$$B_{ijkl}(\mathbf{X}) = \left(\frac{\partial \sigma_{ij}}{\partial \eta_{kl}} \right)_{\text{at } \mathbf{X}} \quad (2)$$

is the elastic stiffness coefficients at the current configuration $\mathbf{X}$. B_{ijkl} is identical to the elastic coefficients, C_{ijkl} , if the crystal is under no-load or linear elastic deformation; however, the B_{ijkl} differs from C_{ijkl} and loses the Voigt symmetry⁽⁸⁾ in the nonlinear elastic deformation. The positiveness of the symmetric part of the matrix, $B_{ijkl}^{\text{sym}} = (B_{ikji} + B_{ijkl})/2$, dominates the crystal stability⁽⁷⁾. The independent components of B_{ijkl}^{sym} can be represented only with the 6×6 matrix, B_{IJ}^{sym} , according to the Voigt notation⁽⁸⁾.

In the present study, the uniaxial tension and compression is applied in the [001] direction. Assuming the isotropy of the transverse directions, the [100] and [010], we get the following conditions for $\det B_{IJ}^{\text{sym}} < 0$.

$$B_{33}(B_{11} + B_{12}) - 2B_{13}^2 < 0 \quad (3)$$

$$B_{11}^2 - B_{12}^2 < 0 \quad (4)$$

$$B_{44} < 0 \quad (5)$$

$$B_{66} < 0 \quad (6)$$

Here the Voigt indices 1, 2 and 3 are set to the crystallographic directions of [100], [010] and [001], respectively. Equations (3) and (4) are referred as spinodal and Born criteria, respectively⁽⁹⁾. In the case of hydrostatic tension and compression, the number of independent components of B_{IJ}^{sym} decreases to lead the following spinodal criteria

$$B_{11} + 2B_{12} < 0 \quad (7)$$

Eqs. (5) and (6) also become identical so that the stability under the hydrostatic deformation is evaluated with the three conditions of Eqs. (4), (5) and (7).

3. Simulation Procedure

Simulations are implemented using the VASP (Vienna *ab-initio* simulation package) developed by Kresse and Hafner⁽¹⁰⁾. The ultrasoft pseudopotential⁽¹¹⁾ is adopted. The core radii of the pseudopotentials for Ni and Al are set to 2.430 a.u. (1.286 Å) and 2.650 a.u. (1.402 Å), respectively. The k -points are sampled according to the Monkhorst-Pack scheme⁽¹²⁾. The exchange correlation term is treated in the formulation of GGA (generalized gradient approximation)⁽¹³⁾. The energy convergence of the electronic state is achieved by the RMM-DIIS scheme (residual minimization method - direct inversion in the iterative subspace)⁽¹⁴⁾. The conditions for each calculation of Ni and Ni₃Al are listed in Table 1. Both calculations use the unit lattice of 4 atoms, fcc for Ni and L1₂ structure for Ni₃Al, as a supercell in the reciprocal space.

The equilibrium lattice length, a_0 , is determined first to set the initial stress zero as the reference of the strain measurement. The values are listed in Table 1. Then the strain increment of $\Delta\epsilon_{33} = \pm 0.03$ or ± 0.01 is applied in the [001] direction for the analyses of the uniaxial tension/compression. The lattice relaxation is implemented by VASP as well as the energy convergence of electron structure. Here, the lateral strain of $\epsilon_{11} = \epsilon_{22}$ is also changed with the interval of $\Delta\epsilon_{11} = 1.0 \times 10^{-4}$ to seek the lateral strain for $\sigma_{11} = \sigma_{22} = 0$. In the analyses of hydrostatic tension/compression, the strain increment of $\Delta\epsilon_{33} = \pm 0.03$ or ± 0.01 is applied isotropically in the [100], [010] and [001], respectively. In all analyses, the stress-strain curves are evaluated in the static deformation pass of the uniaxial tension/compression and hydrostatic tension/compression. The elastic stiffness coefficients necessary for Eqs. (3)–(7) are also numerically calculated

Table 1 Simulation conditions

Material	Ni	Ni ₃ Al
Crystal structure	fcc	L1 ₂
Number of atoms	4	
Cutoff energy (eV)	302	
Number of k points	13 ³	
Lattice constants (Å)	3.52 (theo.)	3.567 (theo.)
	3.5238 (calc.)	3.5748 (calc.)
	0.11% (err.)	0.22% (err.)

from Eq. (2), by applying the small strain perturbation of $\Delta\eta_{ij} = \pm 0.01$ or ± 0.005 at each strain to compute the stress change.

4. Results and Discussion

4.1 [001] uniaxial tension

The relationships between the free energy and strain, the tensile stress and strain are shown in Fig. 1 (a) and (b), respectively. Both Ni and Ni₃Al show the quadratic increase in the free energy. The corresponding stress-strain curves increase monotonically; however, they show a peak around $\varepsilon_{33} = 0.35$ and turn to decrease, suggesting a flexion point in the free energy. The stress-strain curves are almost linear and identical each other up to the strain of 0.12. Then they show the nonlinear elasticity from $\varepsilon_{33} = 0.15$ and slightly deviate since Ni₃Al shows smaller stress than Ni. We can also find subtle concave at $\varepsilon_{33} = 0.03$, as is reported that the fcc crystals show such tendency around the no-load equilibrium under the [001] uniaxial tension⁽¹⁵⁾.

Figure 2 indicates the change in the magnitudes of the left-hand side of Eqs. (3)–(6), or the stability against each criteria. Both Ni and Ni₃Al reach the Born criteria first, then does B_{44} and spinodal ones in turn. Table 2

Fig. 1 [001] uniaxial tension

lists the strain and stress at the point where every instability criterion is satisfied. B_{66} never become negative in the strain range analyzed. The first instability of Born criteria is the point where the magnitude relation between B_{11} and B_{12} inverts, resulting in the bifurcation from the isotropic Poisson's contraction to the anisotropic transverse deformation⁽⁶⁾. The instability against B_{44} would imply the onset of the slip on the (100) or (010) planes. The spinodal criteria could be understood as the instability against cleavage cracking in the [001] direction since it coincides with the peak of the stress-strain curve and B_{33} actually becomes negative in the components of Eq. (3). Here it should be noted that the instability of B_{44} and the spinodal emerge only if the bifurcation to another deformation pass were prohibited after the Born instability. Regarding the critical strain against Born criteria as the elastic

Fig. 2 Lattice stability in the [001] uniaxial tension

Table 2 Instability in the [001] uniaxial tension

Condition	Born		B_{44}		Spinodal	
	ε_{33}	σ_{33}	ε_{33}	σ_{33}	ε_{33}	σ_{33}
Ni	0.11	15.0	0.24	30.6	0.39	35.3
Ni ₃ Al	0.09	12.3	0.30	33.1	0.36	34.0

Unit: GPa

limit, we obtain the theoretical strength of $\epsilon_{33} = 0.11$ and $\sigma_{33} = 15.0$ GPa for Ni, $\epsilon_{33} = 0.09$ and $\sigma_{33} = 12.3$ GPa for Ni₃Al, respectively, under the [001] uniaxial tension.

4.2 [001] uniaxial compression

Figure 3 (a) and (b) illustrate the free energy-strain and the compressive stress-strain curves, respectively. Contrary to the tension, the energy curve has convex around $\epsilon_{33} = -0.20$ in both Ni and Ni₃Al resulting in two extremum, minimum and maximum, in the stress curve. The stress curves are almost identical each other down to the strain of $\epsilon_{33} = -0.06$. Then the Ni shows the minimum at $\epsilon_{33} = -0.11$ while Ni₃Al does at $\epsilon_{33} = -0.12$. After the minimum, the stress goes back despite the continuous compression, showing a local maximum. These cubic-like curves can be explain with the Bain relationship between the bct and bcc/B2 structure in the fcc and L1₂ crystal lattices^{(16),(17)}. The fcc structure of Ni falls into unstable bcc structure at $\epsilon_{33} = -0.20$ and metastable bct structure at $\epsilon_{33} = -0.26$ leading all the stress components zero under the [001] uniaxial compression. The L1₂ structure of Ni₃Al becomes mixed lattice of both bcc and B2 structure so that the stress never vanish.

Figure 4 (a) and (b) indicate the change in the left-

Fig. 3 [001] uniaxial compression

hand side of Eqs. (3)–(6) under the [001] uniaxial compression. The spinodal term and B_{66} become negative in that order in both Ni and Ni₃Al. The strain and stress at each instability point are listed in Table 3. The Born criteria and $B_{44} < 0$ are never satisfied in the analyzed strain range of $-0.42 \leq \epsilon_{33} \leq 0$. The spinodal instability coincides with the minimum of the stress-strain curve, or the peak stress under the compression. However, B_{33} does not become negative in contrast to the tension. That is, the spinodal instability under the compression would not mean the loss of deformation resistance in the loading direction but the phase transformation to another crystal structure. The instability against B_{66} represents the slip along the (100) or (010) plane, while its direction is different from that in tension. There is a report that the fcc lattice of alkali metals shows bifurcation to shear de-

Fig. 4 Lattice stability in the [001] uniaxial compression

Table 3 Instability in the [001] uniaxial compression

Condition	Spinodal		B_{66}	
	ϵ_{33}	σ_{33}	ϵ_{33}	σ_{33}
Ni	-0.11	-5.44	-0.18	-2.0
Ni ₃ Al	-0.12	-5.94	-0.21	-2.43

Unit: GPa

formation by the instability of $B_{66}^{(15)}$. Taking the critical strain against the spinodal instability as the elastic limit, the theoretical strengths of Ni and Ni_3Al are evaluated as $\epsilon_{33} = -0.11$, $\sigma_{33} = -5.44$ GPa and $\epsilon_{33} = -0.12$, $\sigma_{33} = -5.94$ GPa, respectively, under the [001] uniaxial compression.

4.3 Hydrostatic tension and compression

Figure 5 (a) and (b) show the free energy-strain and the stress-strain curves, respectively, under the hydrostatic tension and compression. The energy curves are almost same in both Ni and Ni_3Al , showing single minimum at the no-load equilibrium. The stress curves also resemble each other, having a peak at $\epsilon_{33} = 0.15$ under the tension and no extremum under the compression.

The changes in the left-hand side of Eqs. (4), (5) and (7) are shown in Fig. 6 (a) and (b). All the values drastically surge in the compression, so that the figures mainly focus on the change under the tension. Opposite to the [001] uniaxial tension, Ni reaches the spinodal criteria first, then Born and B_{44} conditions in turn. In the case of Ni_3Al , the spinodal and Born terms become negative simultaneously, then B_{44} follows. The critical strain and stress at each instability are listed in Table 4. The strain of

Fig. 5 Hydrostatic tension and compression

the spinodal criteria coincides with the peak of the stress-strain curve; however, the elastic stiffness coefficient of B_{33} ($= B_{11} = B_{22}$), which represents the resistance against dilatation, never show the negative value. That is, the unstable point, or the peak of the stress-strain, is not the onset of the sublimation by the dilatation but the phase transformation to another crystal structure as similar as the [001] uniaxial compression. Here, the spinodal and Born instability occur at the same strain in Ni_3Al while they are also very close in Ni. Thus there is no denying that the bifurcation to the anisotropic deformation takes place by the Born instability. The theoretical strength under the hydrostatic tension is evaluated at $\epsilon_{33} = 0.15$, $\sigma_{33} = 30.0$ GPa for Ni, $\epsilon_{33} = 0.15$, $\sigma_{33} = 28.3$ GPa for Ni_3Al , respectively, from the spinodal instability.

Fig. 6 Lattice stability in the hydrostatic tension and compression

Table 4 Instability in the hydrostatic tension

Condition	Spinodal		Born		B_{44}	
	ϵ_{33}	σ_{33}	ϵ_{33}	σ_{33}	ϵ_{33}	σ_{33}
Ni	0.15	30.0	0.16	29.8	0.24	26.2
Ni_3Al	0.15	28.3	0.15	28.3	0.24	25.0

Unit: GPa

As mentioned above, no instability arises under the hydrostatic compression on both Ni and Ni₃Al. The stress-strain curve also does not show any minimum so that the theoretical strength cannot be defined. This is due to the assumption of the perfect isotropy in the deformation path; the lattice instability emerges when the isotropy is perturbed. In fact, our another analysis⁽¹⁷⁾ suggests that both Ni and Ni₃Al show the spinodal and B_{66} instability although the stress-strain curve has still no extremum, if they are subjected to anisotropic triaxial compression where the transverse strain of the [100] and [010] is fixed at zero during the [001] compression. That is, the actual hydrostatic compression would face to the spinodal instability due to the declination from the isotropic deformation, then bring about the phase transformation. It is also noteworthy that the extremum of the stress-strain curve could not define the theoretical strength while the lattice stability definitely figures out the value.

5. Conclusion

For the first principle insight on the theoretical strength of Ni and Ni₃Al single crystals, the main composition of the single crystalline Ni-based superalloys, the unit lattices of Ni and Ni₃Al are subjected to the static [001] uniaxial tension/compression and the hydrostatic tension/compression by means of *ab-initio* molecular dynamics (statics) simulations. The lattice stability are discussed at each strain based on the positiveness of the elastic stiffness coefficients. Both Ni and Ni₃Al reach first the instability against the bifurcation to the anisotropic transverse deformation (Born instability) under the [001] uniaxial tension, while they do the spinodal instability against the phase transformation under the [001] uniaxial compression and the hydrostatic tension. From these elastic limits the theoretical strength is evaluated as the critical strain and stress. On the other hand, the theoretical strength could not be defined in the hydrostatic compression since it shows no unstable point nor the local minimum in the stress-strain curve if we assume the perfect isotropy; however, it is also suggested that the spinodal instability emerges if the isotropy is perturbed. All the theoretical strengths of Ni and Ni₃Al analyzed is shown on the $\epsilon_{11} - \epsilon_{33}$ and $\sigma_{11} - \sigma_{33}$ planes as the “yield curve” in Fig. 7. The results of our another analyses⁽¹⁷⁾ for the [001] tension/compression with the zero transverse strain (non-zero transverse stress) are also plotted in the figure. The strengths of Ni and Ni₃Al are very close in the uniaxial tension/compression and the hydrostatic tension, while they deviate if the deformation constraint is forced on the transverse direction. The similar analysis on the various crystal orientation would bring more precise “yield surface” of Ni and Ni₃Al.

Finally, it should be noted that the present study does not involve the electron spin. The effects of the spin mag-

Fig. 7 Stable zone on $\epsilon_{11} - \epsilon_{33}$ and $\sigma_{11} - \sigma_{33}$ planes under the [001] tension and compression

netism on the lattice instability remains as the future work.

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