Dislocation slip and twinning in Ni-based L12 type alloys

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We report theoretical results on dislocation slip and twinning in Ni3 (Al, Ti, Hf) compositions with L12 crystal structures utilizing first-principles simulations. The lattice parameters of Ni3Al, Ni3Al0.75Ta0.25, Ni3Al0.5Ta0.5, Ni3Ta, Ni3Ti and Ni3Al0.75Hf0.25 are calculated, and the crystal structures with lower structural energies are determined. We established the Generalized Stacking Fault Energy (GSFE) and Generalized Planar Fault Energy (GPFE), and calculated stacking fault energies APB (anti-phase boundary) and CSF (complex stacking fault) matched other calculations and experiments. Based on the extended Peierls–Nabarro model for slip and the proposed twin nucleation model, we predict slip and twinning stress and the results show a general agreement with available experimental data. The results show that in the studied intermetallic alloys, twinning stress is lower than slip stress; Ta and Hf ternary addition are substantial to increase flow stress in Ni3Al. The models proposed in the paper provide quantitative understanding and guidelines for selecting optimal precipitate chemistry and composition to obtain higher mechanical strength in Shape Memory Alloys.

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1. Introduction

The quest for the theoretical determination of the stress required for plastic flow via slip and via twinning has been ongoing for many years and has become more important with the need for developing advanced materials [1–9]. Formulas for the stress required for dislocation motion (the slip stress) and the stress required for twin nucleation (the twin stress) have been proposed in our previous research combining atomistic simulations with mesoscale dislocation theory [10,11]. The former calculations rely on the well-known Peierls–Nabarro (P–N) description of the dislocation core, and the more recent calculations extend the P–N model to describe the twin [10]. These theoretical estimates have provided extremely close values compared to experiments in a number of B2 alloys [11]. The twinning mechanism can play an important role in crystals with limited number of independent slip systems, and may readily occur in experiments when the twinning stress magnitude is below the slip stress [10,12–15]. The present paper is on the application of these theories, with modifications to twinning modeling, to several L12 crystals that are of interest in shape memory alloys (SMAs).

Coherent, nontransforming precipitates in advanced SMAs proposed recently with unprecedented properties [16–20] have L12 crystal structures. These precipitates which are Ni-based can occupy a large volume fraction within the austenite or martensite domains. While they do not transform, they influence the transformation characteristics. These coherent precipitates exhibit superior flow resistance compared to the matrix but deform during the transformation to maintain compatibility. The benefit of the precipitates is that they can elevate the slip resistance of the matrix which imparts reversibility and shape memory to the alloy [19,21]. However, no quantitative model has been proposed for the assessment of deformation resistance of these precipitate phases. Many precipitate compositions are possible; in this paper, we specifically focus on the most important ones, the Ni3 (Al, Ti, Ta) compositions with L12 crystal structures. It is not known a priori the relative magnitudes of slip and twinning stress for Ni3 (Al, Ti, Ta) compositions. As mentioned above, the formulation presented in this paper utilizes an extended Peierls–Nabarro framework for slip and twinning utilizing atomistic simulations.

The role of fine precipitates on the shape memory response has been discussed originally by Hornbogen [22] and then by Koval and co-workers [23]. Although the mechanical behavior of the precipitates is not fully understood, they impart beneficial properties as discussed above. The recently proposed SMAs of the Fe variety undergo face centered cubic (fcc) to tetragonal crystal transformations where both the austenite and martensite phases are disordered [19,21,24]. The presence of coherent precipitates has been proposed to impart surprising thermoelastic shape
memory response in these alloys. The details of the shape memory response is outside the scope of this paper, but the modification of mechanical properties due to Ta and Hf additions on strengthening of these precipitates is within the scope of our investigation.

Recent studies of electronic structure calculations have developed an accurate description of the fault energy curves in metallic alloys. Different crystal structures, slip and twin planes and directions have been simulated. The original calculations have focused on the determination of ideal stresses [9], and more recently utilizing dislocation mechanics at the mesoscale a better estimation of flow resistance in agreement with experiments have been achieved [10,11]. Recent developments incorporated a better description of the dislocation core particularly for the case of fractional or partial dislocations. The results show excellent agreement with experiments for twinning [10] and slip [11] in a number of intermetallic alloys.

In this paper, we present the modeling efforts for slip and twinning for Ni$_3$(Al, Ti, Ta, Hf) compositions with L1$_2$ crystal structures. The lattice parameters are studied as well as the crystal structure for the ground state by comparing L1$_2$ and other crystal structures. The modeling efforts require shear moduli and accurate description of GSFE and GPFE curves with internal relaxation. The GSFE curves represent the Generalized Stacking Fault Energy which is an accurate description of slip in the case of partial or full dislocation slip [25]. The GPFE curves represent the energy landscape associated with partial dislocations and describe the layer by layer growth of the twin [26]. Because the path leading to the twin formation deviates from that of slip, the GPFE and GSFE curves, hence the corresponding stress levels for the two mechanisms are not the same. We discuss this in detail for the materials of interest in this study.

2. Simulation methods

We utilized Density Functional Theory (DFT) to investigate the crystal structure energy and establish GSFE and GPFE curves. The first-principles total-energy calculations were carried out using the Vienna ab initio Simulations Package (VASP) [27,28] with the projector augmented wave (PAW) method and the generalized gradient approximation (GGA). In our calculations, Monkhorst-Pack 9 × 9 × 9 k-point meshes were used for the Brillouin-zone integration. Ionic relaxation was performed by a conjugate gradient algorithm and stopped when absolute values of internal forces were smaller than 5 × 10$^{-3}$ eV/Å. The energy cut-off of 500 eV was used for the plane-wave basis set. The total energy was converged to less than 10$^{-5}$ eV per atom. We have used an n-layer based cell to calculate fault energies to generate GSFE and GPFE curves for studied materials. We assessed the convergence of the GSFE and GPFE energies with respect to increasing n, which indicates that the fault energy interaction in adjacent cells due to periodic boundary conditions will be negligible. The convergence is ensured once the energy calculations for n and n + 1 layers yield the same GSFE and GPFE. In the present study, we performed a full atomic relaxation to establish the GSFE and GPFE. During full relaxation the atoms can move in the out of plane and normal to the slip and twin plane although these displacements are small relative to the shear displacement. This relaxation process caused a small additional atomic displacement $r = \sqrt{r_x^2 + r_y^2 + r_z^2}$ deviating from the Burgers vector. Thus, the total fault displacement is not exactly equal to u but involves additional r. The total energy of the deformed (faulted) crystal was minimized during this relaxation process through which atoms can avoid coming too close to each other during shear [29–31].

3. Results and discussion

We studied several Ni-based L1$_2$ type binary and ternary alloys: Ni$_3$Al, Ni$_3$Al$_{0.5}$Ta$_{0.5}$, Ni$_3$Al$_{0.75}$Ta$_{0.25}$, Ni$_3$Ta, Ni$_3$Ti and Ni$_3$Al$_{0.75}$Hf$_{0.25}$. We note that theoretical studies of L1$_2$ Ni$_3$Al (crystal structure, dislocation slip and twin) can be found in literature [32–39], Ni$_3$Ta and Ni$_3$Ti having the L1$_2$ crystal structure are similar to Ni$_3$Al, and thus, in this paper we will only report the results in Tables 1 and 2 without giving calculation details for these three materials. Instead, the ternary alloys Ni$_3$Al$_{0.5}$Ta$_{0.5}$ and Ni$_3$Al$_{0.75}$Ta$_{0.25}$ will be focused in the paper including the determination of crystal structure, prediction of dislocation slip and twin nucleation stress (Section 3.1). Since the atomic arrangements of Ni$_3$Al$_{0.75}$Hf$_{0.25}$ are similar to those of Ni$_3$Al$_{0.75}$Ta$_{0.25}$, we will only report the calculated results for this material in Tables 1 and 2.

We plot the predicted dislocation slip and twinning stress of the Ni-based L1$_2$ type alloys variation with the composition x in Fig. 1. The composition x can be considered as the concentration of R in Ni$_3$Al$_{1-x}$R$_x$ for R = Ta, Hf and Ti. We note that for all these alloys, the twinning stress (circle) is lower than slip stress (square), which indicates that twinning is more favorable than dislocation slip as the deformation mechanism. Twinning is experimentally observed and theoretically found in L1$_2$ alloys as a significant deformation mechanism [32,40–44]. Although the values of slip stress are higher than those of twinning, the difference is not significant and the dislocation slip can be activated due to the sufficiently high local stress. Thus, dislocation slip is also often observed experimentally in L1$_2$ alloys [45–50]. For the alloy Ni$_3$Al$_{1-x}$Ta$_x$ in Fig. 1, we note that both slip and twinning stress increase as composition x becomes larger, but after x = 0.5, they are increasing slowly and reach maximum values at x = 1. In addition, by comparing the Ni$_3$Ti and Ni$_3$Ta, we note that the values of slip and twinning stress in Ni$_3$Ta are higher than Ni$_3$Ti by around 9%, so Ta should be more suitable than Ti for obtaining high mechanical strength in SMAs. Furthermore, we note that the values of slip and twinning stress in Ni$_3$Al$_{0.75}$Hf$_{0.25}$ are higher than Ni$_3$Al$_{0.75}$Ta$_{0.25}$ by around 15%, and very close to those of Ni$_3$Al$_{0.5}$Ta$_{0.5}$. This indicates that the addition of Hf should be more efficient than other chemistries to increase the deformation resistance in SMAs.

3.1. Ni$_3$Al$_{0.5}$Ta$_{0.5}$

3.1.1. Crystal structure in Ni$_3$Al$_{0.5}$Ta$_{0.5}$

In order to study the crystal structure of Ni$_3$Al$_{0.5}$Ta$_{0.5}$ (atomic ratio is 6:1:1), two different supercells termed ‘L1$_2$-like’ and ‘DO$_{22}$-like’ are constructed [61]. Both these supercells consist of two L1$_2$ subcells with total eight atoms [61,62]. The L1$_2$-like supercell (Fig. 2a) can be constructed from a supercell containing two L1$_2$ Ni$_3$Al subcells, but the Al occupying the middle corners of the supercell and shared by the two subcells, are replaced by Ta. Since there are six Ni at the face centers in each subcell (three Ni atoms), altogether there are six Ni atoms in the L1$_2$-like supercell. In addition, eight Al occupy the top and bottom corners and four Ta

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**Table 1** Calculated lattice parameter and Burgers vector are compared to other calculations and experimental data in Ni-based L1$_2$ type alloys.

<table>
<thead>
<tr>
<th>Materials (L1$_2$)</th>
<th>Lattice parameter (Å)</th>
<th>Burgers vector (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Experiments</td>
<td>This study</td>
</tr>
<tr>
<td>Ni$_3$Al</td>
<td>3.58</td>
<td>3.57</td>
</tr>
<tr>
<td>Ni$<em>3$Al$</em>{0.5}$Ta$_{0.25}$</td>
<td>3.60</td>
<td>3.61</td>
</tr>
<tr>
<td>Ni$<em>3$Al$</em>{0.75}$Ta$_{0.25}$</td>
<td>3.62</td>
<td>3.625</td>
</tr>
<tr>
<td>Ni$_3$Ta</td>
<td>3.62</td>
<td>3.68</td>
</tr>
<tr>
<td>Ni$_3$Ti</td>
<td>3.62</td>
<td>3.62</td>
</tr>
<tr>
<td>Ni$<em>3$Al$</em>{0.75}$Hf$_{0.25}$</td>
<td>3.62</td>
<td>3.615</td>
</tr>
</tbody>
</table>
occupy the middle corners, so there is total one Al atom and one Ta atom. Therefore, in the supercell the atomic ratio is 6:1:1. The D0$_{22}$-like supercell (Fig. 2b) is similar to the L1$_2$-like supercell and possesses the atomic ratio of 6:1:1. The difference between these two supercells is that the Ta in the D0$_{22}$-like supercell is at the body center (occupy Ni sites) instead of being at the middle corners (occupy Al sites) in the L1$_2$-like supercell.

To determine the stability of the two different structures for Ni$_3$Al$_{0.5}$Ta$_{0.5}$, we calculated total energy as a function of lattice parameter of the D0$_{22}$-like structure and the L1$_2$-like structure shown in Fig. 3. We note that Ni$_3$Al$_{0.5}$Ta$_{0.5}$ in the L1$_2$-like structure is energetically favored over the D0$_{22}$-like structure, because in the entire range of lattice parameters the total energies of the L1$_2$-like structure are lower than those of the D0$_{22}$-like structure by near 0.2 eV per formula unit. These results indicate that when we consider Ni$_3$Al$_{0.5}$Ta$_{0.5}$ as the ternary additions of Ta in Ni$_3$Al, the Ta will preferentially occupy the Al sites (L1$_2$-like structure) over than the Ni sites (D0$_{22}$-like structure). Our calculations are consistent with Ni$_3$Al$_{0.5}$V$_{0.5}$ \cite{61} and Ni$_3$Al$_{0.5}$Nb$_{0.5}$ \cite{63}, where the L1$_2$-like structure is more stable than other structures in these two materials. Therefore, in the following studies of dislocation slip and Table 2

<table>
<thead>
<tr>
<th>Materials (L1$_2$)</th>
<th>GSFE (slip) (mJ/m$^2$)</th>
<th>APB</th>
<th>GPFE (twin) (mJ/m$^2$)</th>
<th>Slip stress (MPa)</th>
<th>Twinning stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$Al</td>
<td>276</td>
<td>682</td>
<td>241</td>
<td>236 [56]</td>
<td>223</td>
</tr>
<tr>
<td>Ni$<em>3$Al$</em>{0.75}$Ta$_{0.25}$</td>
<td>873</td>
<td>1134</td>
<td>552</td>
<td>396 [58]</td>
<td>615</td>
</tr>
<tr>
<td>Ni$<em>3$Al$</em>{0.5}$Ta$_{0.5}$</td>
<td>635</td>
<td>1331</td>
<td>320</td>
<td>599 [60]</td>
<td>505</td>
</tr>
<tr>
<td>Ni$_3$Ta</td>
<td>330</td>
<td>856</td>
<td>–</td>
<td>–450 [50]</td>
<td>–577</td>
</tr>
<tr>
<td>Ni$_3$Ti</td>
<td>627</td>
<td>1378</td>
<td>460</td>
<td>468 [60]</td>
<td>516</td>
</tr>
<tr>
<td>Ni$<em>3$Al$</em>{0.5}$Hf$_{0.25}$</td>
<td>902</td>
<td>1177</td>
<td>612</td>
<td>–</td>
<td>734</td>
</tr>
</tbody>
</table>

The dash indicates that experimental data were not available for comparison.

Fig. 1. Predicted dislocation slip and twinning stress of the Ni-based L1$_2$ type alloys, Ni$_3$Al$_{1-x}$R$_{x}$ for R = Ta, Hf and Ti, variation with composition x. The stress values are shown in Table 2.

Fig. 2. Two crystal structures of Ni$_3$Al$_{0.5}$Ta$_{0.5}$ (a) L1$_2$-like structure and (b) D0$_{22}$-like structure. There are total eight atoms in each structure and the atomic ratio is 6:1:1.

Fig. 3. Total energy as a function of lattice parameter for D0$_{22}$-like (read line) and L1$_2$-like (blue line) Ni$_3$Al$_{0.5}$Ta$_{0.5}$. The total energies of the L1$_2$-like structure are lower than those of the D0$_{22}$-like structure by near 0.2 eV per formula unit. The calculated lattice parameter is compared to other calculations and experiments shown in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
twin nucleation in Ni₃Al₀.5Ta₀.5, we established the GSFE and GPFE curves for L1₂-like structure as it has greater stability.

3.1.2. Dislocation slip (GSFE) in L1₂-like Ni₃Al₀.5Ta₀.5

In this study, we investigate the slip system [111]<110> for Ni₃Al₀.5Ta₀.5, which is often experimentally observed in L₁₂ crystal structure [34,36,64,65]. The <110>-superdislocation in the [111] slip plane can dissociate into two 1/2<110> superpartials with formation of APB (anti-phase boundary) energy. The superpartial can further dissociate into two Shockely partials 1/6<110> described later. The {110} planes composed of only Ni atoms (shown in brown dashed line) can further dissociate into two 1/2<110> connected by CSF (complex stacking fault) energy [32,35,66–68]. This process results in a fourfold dissociation in Eq. (1):

\[
[T10] = \frac{1}{6}[Z11] + CSF + \frac{1}{6}[T2T] + APB + \frac{1}{6}[Z11] + CSF
+ \frac{1}{6}[T2T]
\]

(1)

Fig. 4 shows a top view from the direction perpendicular to the [111] slip plane with three-layer of atoms stacking in Ni₃Al₀.5Ta₀.5. Three different sizes of atoms indicate three successive (111) layers from the top view, which is similar to fcc metals. However, certain symmetries existing in fcc lattice are not found in L₁₂ lattice. We note that (110) planes composed of only Ni atoms (shown in brown dashed line in Fig. 4) are not planes of mirror-symmetry in the L₁₂ lattice, which is different with the case of fcc lattice where every (110) plane has this symmetry [69]. Therefore, the superdislocation [T10] (brown arrow) in L₁₂ lattice must dissociate into four superpartials 1/6<211> (blue arrow) corresponding to Eq. (1). While in fcc lattice, the full dislocation 1/2[T10] dissociates into two partials 1/6<211> [35,70]. Two types of planar defects CSF and APB are formed with the dissociation of superdislocation [T10] in L₁₂, which does not exhibit in fcc metals. A CSF is produced when the in-plane atoms and all atoms above are shifted along the Burgers vector 1/6[Z11] (a → b and c → d in Fig. 4). An APB is formed when the in-plane atoms and all atoms above are shifted along the Burgers vector 1/2[T10] (a → c and c → e in Fig. 4). The points a, b, c, d and e correspond to the stable (metastable) positions in the GSFE curve described later.

Fig. 5 shows the slip plane (111) (shaded violet) and slip direction [TT2] (red arrow) in L₁₂-like Ni₃Al₀.5Ta₀.5. The lattice parameter a is calculated as 3.62 Å in Fig. 3, which is in a good agreement with experimental measurements (Table 1).

The slip energy barriers (unstable stacking fault energies) and planar defect energies (CSF and APB) are all characterized by the GSFE curve, which is calculated when one half crystal is shifted relative to the other in the slip plane along the slip direction [12]. The 1/6[TT2] (111) case of L₁₂-like Ni₃Al₀.5Ta₀.5 is illustrated in Fig. 6 showing the configuration of slip in the (111) with dissociation 1/6[TT2]. Fig. 6a is the perfect L₁₂ lattice before shear, while Fig. 6b is the lattice after shear by one Burgers vector, b = 1/6[TT2] = 1.48 Å, in the slip plane. All fault energies can be computed as a function of shear displacement, u, and are determined relative to the energy of the undeformed L₁₂.

The calculated GSFE curve in the slip system 1/6<110> is shown in Fig. 7. The points a, b, c, d and e correspond to the stable (metastable) positions in the GSFE curve (see atomic configuration in Fig. 4). The calculated stacking fault energies are compared well to other calculations and experimental data in Table 2. The Peierls stress of L₁₂-like Ni₃Al₀.5Ta₀.5 is calculated as 603 MPa (Table 2) utilizing our extended Peierls–Nabarro model described in Appendix A.

3.1.3. Twin nucleation (GPFE) in L1₂-like Ni₃Al₀.5Ta₀.5

We calculated the GPFE curve of the L₁₂-like Ni₃Al₀.5Ta₀.5 by successive shear of every (111) plane over 1/6[TT2] twinning partial (the twinning Burgers vector b = 1/6[TT2] = 1.48 Å) [10,12]. Fig. 8a shows the perfect lattice of L₁₂-like Ni₃Al₀.5Ta₀.5, while Fig. 8b is the lattice with a three-layer twin after shearing 3b (shown in a red arrow) in successive (111) planes (twin plane is marked with a brown dashed line). The atomic arrangement is viewed from the [110] direction.

The calculated energy landscape (GPFE) for a three-layer twin formation in L₁₂-like Ni₃Al₀.5Ta₀.5 is shown in Fig. 9. The calculated energies associated to the twin process are shown in Table 2. The critical twin nucleation stress of L₁₂-like Ni₃Al₀.5Ta₀.5 is calculated...
Fig. 6. Dislocation slip in the (111) plane with dislocation $\frac{1}{6}[112]$ of L1$_2$-like Ni$_3$Al$_{0.5}$Ta$_{0.5}$. (a) The perfect L1$_2$-like lattice observed from the $[\overline{1}10]$ direction. The slip plane (111) is marked with a brown dashed line. (b) The lattice after a rigid shear with dislocation $\frac{1}{6}[112]$, $u$, shown in a red arrow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. The GSFE curve of the slip system $1/6<112>$ in L1$_2$-like Ni$_3$Al$_{0.5}$Ta$_{0.5}$. The dislocation $[\overline{1}10]$ can dissociate into four superpartials $1/6<112>$ connected by stacking fault energies CSF and APB. The calculated CSF, APB and unstable stacking fault energies are shown in Table 2. The points a, b, c, d and e correspond to the stable (metastable) positions in the GSFE curve (see atomic configuration in Fig. 4).

Fig. 8. (a) The perfect L1$_2$-like lattice viewed from the $[\overline{1}10]$ direction. Twin plane (111) is marked with a brown dashed line. (b) The lattice with a three-layer twin after shearing 3b along $1/6[112]$, shown in a red arrow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 9. The GPFE curve in the twin plane (111) with twin dislocation $1/6[112]$ of L1$_2$-like Ni$_3$Al$_{0.5}$Ta$_{0.5}$. The shear displacement, $u$, is normalized by the twinning Burgers vector $b = 1/6[112]$. The calculated fault energies are shown in Table 2.
as 490 MPa (Table 2) utilizing our developed twin nucleation model described in Appendix B.

3.2. Ni₃Al₀.₇₅Ta₀.₂₅

3.2.1. Crystal structure in Ni₃Al₀.₇₅Ta₀.₂₅

Similar to the case of Ni₃Al₀.₅Ta₀.₅, we constructed two different supercells 'L₁₂-like' and 'D₀₂₂-like' to study the crystal structure of Ni₃Al₀.₇₅Ta₀.₂₅ (atomic ratio is 12:3:1). Both these supercells consist of four L₁₂ subcells with total 16 atoms. Fig. 10a shows the L₁₂-like structure and the view from the direction [010]. This supercell can be created from a supercell containing four L₁₂ Ni₃Al subcells, but the Al at the face centers shared by these four subcells, are replaced by Ta. Since there are six Ni at the face centers in each subcell (three Ni atoms), altogether there are twelve Ni atoms in the L₁₂-like supercell. In addition, there are six Al (6/8 Al atom) and two Ta (2/8 Ta atom) occupying the corners in each subcell, so the total number of atoms for Al and Ta is three and one, respectively. Therefore, in the supercell the atomic ratio is 12:3:1. The D₀₂₂-like supercell (Fig. 10b) is similar to the L₁₂-like supercell and possesses the same atomic ratio of 12:3:1. The difference between these two supercells is that the Ta in D₀₂₂-like supercell is at the body center (occupy Ni sites) instead of being at the middle corners (occupy Al sites) in L₁₂-like supercell.

Fig. 10. Two crystal structures of Ni₃Al₀.₇₅Ta₀.₂₅ (a) L₁₂-like structure and the view from [010] direction. (b) D₀₂₂-like structure and the view from [010] direction.
We calculated total energy as a function of lattice parameter of D022-like and L12-like to determine the stability of these two different structures in Ni3Al0.75Ta0.25 (Fig. 11). Similar to the case of Ni3Al0.75Ta0.5, Ni3Al0.75Ta0.25 in the L12-like structure has lower total energies than those of the D022-like structure by near 1.2 eV per formula unit. Thus, Ni3Al0.75Ta0.25 in the L12-like structure is energetically favored over the one in the D022-like structure. These results are expected when we consider the Ni3Al0.75Ta0.25 as the ternary additions of Ta in Ni3Al, the Ta will preferentially occupy the Al sites (L12-like structure) over than the Ni sites (D022-like structure) [61,63,71]. Therefore, in the following studies of dislocation slip and twin nucleation in Ni3Al0.75Ta0.25, we established the GSFE and GPFE curves for L12-like structure as it is more energetically stable.

3.2.2. Dislocation slip (GSFE) in L12-like Ni3Al0.75Ta0.25

Similar to the dislocation slip in Ni3Al0.5Ta0.5, the slip system \(\{111\}<110>\) is considered to study the dislocation slip in Ni3Al0.75Ta0.25. Fig. 12 shows the superdislocation \(<110>\) in the \(\{111\}\) slip plane dissociated into four superpartials 1/6\(<111>\) slip plane dissociated into four superpartials 1/6\(<111>\) with formation of CSF and APB energies (see Eq. (1)).

Fig. 13 shows the unit cell of L12-like Ni3Al0.75Ta0.25 with the slip plane \(\{111\}\) (shaded violet) and slip direction \(\{TTz\}\) (red arrow). The lattice parameter \(a\) is calculated as 3.60 Å in Fig. 11, which is in a good agreement with experimental measurements (Table 1).

The slip system 1/6\(\{TTz\}\)(111) of L12-like Ni3Al0.75Ta0.25 is illustrated in Fig. 14 with the slip plane (111) and dislocation 1/6\(\{TTz\}\). Fig. 14a is the perfect L12-like lattice before shear, while Fig. 14b is the lattice after shear by one Burgers vector, \(b = \sqrt{6}/6a = 1.47A\), in the slip plane.

We calculated the GSFE curve in the slip system 1/6<112>(111) of L12-like Ni3Al0.75Ta0.25 shown in Fig. 15. The points a, b, c, d, e correspond to the stable (metastable) positions in the GSFE curve (see atomic configuration in Fig. 12). The calculated stacking fault energies are compared well to other calculations and experimental data in Table 2. The Peierls stress of L12-like Ni3Al0.75Ta0.25 is calculated as 317 MPa in Table 2.

3.2.3. Twin nucleation (GPFE) in L12-like Ni3Al0.75Ta0.25

We calculated the GPFE curve of L12-like Ni3Al0.75Ta0.25 by successive shear of every (111) plane over 1/6\(\{TTz\}\) twinning partial (the twinning Burgers vector \(b = \sqrt{6}/6a = 1.47A\)). Fig. 16a shows the perfect lattice of L12-like Ni3Al0.75Ta0.25, while Fig. 16b is the lattice with a three-layer twin after shearing 3b (shown in a red arrow) in successive (111) planes (twin plane is marked with a brown dashed line). The atomic arrangement is viewed from the (T10) direction.

The calculated energy landscape (GPFE) for a three-layer twin formation in L12-like Ni3Al0.75Ta0.25 is shown in Fig. 17. The calculated energies associated to the twin process, and the critical twin nucleation stress of 395 MPa are shown in Table 2.
4. Conclusions

In this study, we predicted the dislocation slip and twinning stresses for Ni$_3$(Al, Ti, Ta, Hf) compositions with L1$_2$ crystal structures based on the extended Peierls–Nabarro model for slip and the proposed twin nucleation model. These models provide quantitative understanding and guidelines for selecting optimal precipitate chemistry and composition to obtain higher mechanical strength in SMAs. The calculated results support the following conclusions:

1. The twinning stress for the intermetallic Ni$_3$(Al, Ta) and Ni$_3$(Al, Hf) compositions were found to be lower compared to the slip stress.

2. The increase in flow stress with increasing Ta and Hf contents in Ni$_3$Al is substantial. With addition of Ta (in the range $x = 0$ to 0.5 for Ni$_3$Al(1/3)xTa$^{x}$) the slip stress increased from 164 MPa to 603 MPa and the twinning stress from 148 MPa to 490 MPa, respectively. For the case of Hf addition, the increase in stress levels was more significant; they were as high 588 MPa and 456 MPa for slip and twinning respectively corresponding to the $x = 0.25$ for Ni$_3$Al(1/3)xHf$^{x}$ case.

3. Internal relaxation of atoms was allowed in obtaining the energy landscapes for slip-GSFE and for twinning-GPFE. Both the twin and slip planes were (111) and the Burgers vector...
was <112> type. The theoretical APB (anti-phase boundary) energy and CSF (complex stacking fault) energy values matched the experiments.

(4) The predicted flow stress values are in general agreement with experiments for the cases where experimental data is available. There appears to be considerable scatter in experimental values; however, the theory captures the trends accurately.

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Appendix A. Prediction of Peierls stress for dislocation slip by extended P–N model

To calculate the Peierls stress, $\tau_p$, for dislocation slip, a potential energy of displacement associated with the dislocation movement, misfit energy $E_s(u)$, was determined [72,73]. This energy depends on the position of the dislocation line within a lattice cell and reflects the lattice periodicity, thus it is periodic [74,75]. The $E_s(u)$ is defined as the sum of misfit energies between pairs of atomic planes and is calculated from the GSFE at the local disregistry [31]:

$$E_s(u) = \sum_{m=-\infty}^{\infty} \gamma f(ma' - u)$$

(A.1)

where, $\gamma[f(x)]$ is determined from GSFE curve, $a'$ is the periodicity of $E_s$, and defined as the shortest distance between two equivalent atomic rows in the direction of the dislocation displacement, $f(x)$ is the disregistry function representing the relative displacement of the two half crystals in the slip plane along the $x$ direction [3,5,76] and $u$ is the position of dislocation line.

The disregistry function $f(x)$ can be described in Eq. (A.2) by considering the multiple partials:

$$f(x) = \frac{b}{\pi} \left[ \arctan \left( \frac{x}{\xi} \right) + \arctan \left( \frac{x - d_C}{\xi} \right) + \arctan \left( \frac{x - (d_C + d_A)}{\xi} \right) \right] + 2b$$

(A.2)

Fig. A.1 shows the normalized $f(x)/b$ variation with $x/\xi$ in L1$_2$-like Ni$_3$Al$_{0.75}$Ta$_{0.25}$, where $\xi$ is the half width of the dislocation core. The separation distances, $d_C = 11.4$ Å and $d_A = 14.9$ Å, of partial dislocations are calculated using the force balance between attraction due to fault energies and elastic repulsion of partial dislocations [77–79].

After determining the $f(x)$ and approximating the GSFE curve by a sinusoidal series function (Fig. 15), we can calculate the misfit energy in Eq. (A.1). Fig. A.2 shows the misfit energy $E_s(u)$ variation with the lattice period $a'$ for the superdislocation $\{10\}$ of Ni$_3$Al$_{0.75}$Ta$_{0.25}$. Therefore, the Peierls stress $\tau_p$ can be calculated by the maximum of $(1/b)(dE_s(u)/du)$. Two quantities $(E_s)_{\gamma/2}$ and $(E_s)_{\gamma/p}$ in the plot are denoted. The $(E_s)_{\gamma/2}$ represents the minimum of $E_s(u)$ function and provides an estimate of the core energy of dislocations. The $(E_s)_{\gamma/p}$ is defined as the Peierls energy, which is the amplitude of the variation of $E_s(u)$ and the barrier required to move dislocations [75,11].

Appendix B. Prediction of critical twin nucleation stress by twin nucleation model

We have developed a twin nucleation model to predict the critical twin nucleation stress in alloys (see details in Ref. [10]). In the present study, the twin nucleation stress for Ni-based alloys was predicted utilizing this model. We determined the total energy involved in the twin nucleation as follows:

![Fig. 17. The GPFE curve in the twin plane (111) with the twin dislocation $b = 1/6[T\overline{T}2]$ of L1$_2$-like Ni$_3$Al$_{0.75}$Ta$_{0.25}$. The shear displacement, $u$, is normalized by the twinning Burgers vector $b = 1/6[T\overline{T}2]$. The calculated fault energies are shown in Table 2.](image1)

![Fig. A.1. The disregistry function $f(x)$ for the superdislocation $\{10\}$ dissociated into four partials $1/6[211]$ in L1$_2$-like Ni$_3$Al$_{0.75}$Ta$_{0.25}$. The separation distances of the partial dislocations are calculated as $d_C = 11.4$ Å and $d_A = 14.9$ Å.](image2)

![Fig. A.2. Misfit energy $E_s(u)$ for the superdislocation $\{110\}$ of Ni$_3$Al$_{0.75}$Ta$_{0.25}$.](image3)
where, $E_{\text{int}}$ is the twin dislocations interaction energy, $E_{\text{GPFE}}$ is the twin boundary energy (GPFE), $E_{\text{line}}$ is the twin dislocations line energy and $W$ is the applied work; $\mu$ is the shear modulus in the twinning system, $b$ is the Burgers vector of the twinning dislocation, $v$ is the Poisson's ratio, $\theta$ is the angle between the Burgers vector and the dislocation line, $L$ is the dimensions of the crystal containing the twin; $\tau$ is the applied shear stress and the minimum to form a twin is called critical twin nucleation stress, $\tau_{\text{crit}}$; $N$ is the number of twin nucleation layers, $h$ is the twin thickness and $d_i$ is the equilibrium spacing between two adjacent twinning dislocations $i$ and $i + 1$ corresponding to the minimum total energy. Fig. B.1 shows a schematic of twin formation in Ni$_3$Al$_{0.75}$Ta$_{0.25}$, where $N = 3$ and $i = 1, 2$ are determined corresponding to Eq. (B.1). We note that depending on the crystal structure and twin system, the number of twin nucleation layers, $N$, can have values other than 3, so we keep $N$ in the following equations for general cases.

The disregistry function $f(x)$ considering the interaction of multiple twinning dislocations is derived as the following:

\[
E_{\text{total}} = E_{\text{int}} + E_{\text{GPFE}} + E_{\text{line}} - W = \frac{\mu b^2}{4\pi(1 - \nu)} \left(1 - \nu \cos^2 \theta\right) \sum_{m=1}^{N} \left(\sum_{i=1}^{m} \ln \frac{L}{d_i} + \sum_{i=2}^{m} \frac{\ln L}{d_i} + \ldots + \sum_{i=N}^{m} \frac{\ln L}{d_i} \right) + \sum_{m=m}^{\infty} \frac{\gamma_{\text{GPFE}} (mb)b}{2(1 - \nu)} \left(1 - \nu \cos^2 \theta\right) - \sum_{i=1}^{N-1} \tau_0 \sin \theta d_i, \quad i = 1, 2, 3, \ldots, N-1,
\]

\[
(B.1)
\]

\[
f(x) = \frac{b}{2} + \frac{b}{N\pi} \left(\tan^{-1} \left(\frac{x}{\zeta}\right) + \tan^{-1} \left(\frac{x - d_1}{\zeta}\right) + \ldots + \tan^{-1} \left(\frac{x - d_1 - d_2 - \ldots - d_{i-1}}{\zeta}\right)\right), \quad i = 1, 2, 3, \ldots, N-1,
\]

\[
(B.2)
\]

To determine the critical stress, $\tau_{\text{crit}}$, we minimized the total energy for the twin nucleation, $E_{\text{total}}$, with respect to $d_i$:

\[
\frac{\partial E_{\text{total}}}{\partial d_i} = 0, \quad i = 1, 2, 3, \ldots, N-1.
\]

\[
(B.3)
\]

By numerically solving the above set of $N - 1$ equations, the critical twinning stress can be determined as the minimum value of the applied stress where these equations satisfy. We note that all parameters involved in the equations Eqs. (B1)–(B3) can be calculated from atomistic simulations, and no fitting parameter from experimental measurements is needed. Therefore, we
predict the twin nucleation stress for the Ni-based alloys in Table 2.

References

[53] Tanaka Y, Himuro Y, Kainuma R, Sutou Y, Omori T, Ishida K. Ferrous poly-


