The effect of the elastic energy on the shape and orientation relations of η-Ni3Ti precipitates in lath martensite

Mati Shmulevitch\textsuperscript{a}, Sigalit Ifergane\textsuperscript{a}, Noam Eliaz\textsuperscript{b,}\textsuperscript{*}, Roni Z. Shneck\textsuperscript{c,}\textsuperscript{*}

\textsuperscript{a} Nuclear Research Center Negev, POB 9001, Beer Sheva 84190, Israel
\textsuperscript{b} Department of Materials Science and Engineering, Tel Aviv University, Ramat Aviv, Tel Aviv 6997801, Israel
\textsuperscript{c} Department of Materials Engineering, Ben-Gurion University of the Negev, POB 653, Beer Sheva 8410501, Israel

A R T I C L E   I N F O
Article history:
Received 28 March 2022
Received in revised form 14 June 2022
Accepted 17 June 2022
Available online 20 June 2022

Keywords:
Elastic interaction energy
Lath martensite
Precipitation hardening
Custom 465\textsuperscript{®} stainless steel

A B S T R A C T
Understanding the elastic interaction between the precipitates may assist in controlling their distribution and help design new steels with enhanced mechanical properties. Custom 465\textsuperscript{®} stainless steel contains only η-Ni3Ti precipitates, making it an ideal steel to study the interaction and orientation relation (OR) between precipitates, which are known to grow in arrays parallel to the four closed-packed axes, <111>\textsubscript{bcc}, and closed-packed planes, (110)\textsubscript{bcc}, of the matrix. This forms 144 possible orientation pairs, raising the question whether there are preferred relations between neighboring precipitates.

In this work we tackle this question by calculating the elastic fields and interaction between η-Ni3Ti precipitates in bcc lath martensite in order to study the effect of elastic energy on the shape and orientation of the precipitates. The results of the calculations are compared to transmission electron microscopy (TEM) observations of Custom 465\textsuperscript{®} stainless steel in different aging conditions. The calculations predict that the η-Ni3Ti precipitates will favor an ellipsoidal morphology with a high aspect ratio. Experimentally, needle-shaped precipitates of $b/a=3$ are observed in the steel in the peak-aged condition. Careful examination of the 144 possible orientation pairs reveals that they may be classified into five groups of crystallographically independent pairs of precipitates. The interaction energy of two precipitates reaches up to ~7% of the self-energy, higher than the typical interaction energy of precipitates in Ni-based superalloys. Here, the ORs between the precipitate is expected to occur in a more sophisticated manner along the four $<111>$ branches. We provide evidence that effective interactions exist inside branches and between inter-penetrating branches inclined at 109.5°, although they are not very clear since not all of the favored sites are occupied.

© 2022 Elsevier B.V. All rights reserved.

1. Introduction

Precipitation hardened steels are used in many applications, e.g. aircraft landing gear, rocket cases, high-performance shafts and tubes, and high-strength fasteners [1–4]. Moreover, understanding the relation between the precipitates may assist in controlling their distribution and help design advanced steels. In view of their wide applications, advanced structural steels are essential for sustainable future, reducing the environmental pollution in the steelmaking industry [1,2].

It has been realized that the body-centered cubic (bcc) ferritic/martensitic steels are ideal materials for strengthening by coherent nanoparticles [2]. Quenching low-carbon steel forms lath martensite with a bcc structure, where a high density of precipitates grow during the aging process; this appears in steels such as traditional and advanced maraging steels (e.g., Custom 465\textsuperscript{®}), ultrahigh-strength steels, etc. [3–13]. Among the precipitates that may nucleate during the aging process, hexagonal η-Ni3Ti precipitates are common and effective strengthening phases [1]. Recently, a maraging steel that was characterized by atom probe tomography (APT) showed fast formation of η-Ni3Ti precipitates at the beginning of the aging process, which could act as nucleation sites for latter precipitation of Ni3Al and Ni3Mo precipitates [9]. Ti additions have the highest strengthening effect by precipitating η-Ni3Ti in some maraging steels [10,14]. Addition of Cu to Fe–Cr–Ni–Al–Ti maraging stainless steel provides nucleation sites for the precipitation of Ni3(Ti,Al) by forming independent Cu clusters [15]. Furthermore, the synergistic effects among Mo, Ti, and Cr on nanoscale precipitation have been studied by APT and transmission electron microscopy (TEM) [16–18]. The APT results indicate that Mo partitions to the η-
$\text{Ni}_3\text{Ti}$ precipitate core in an early stage of precipitation, doubling the number density of $\eta$-$\text{Ni}_3\text{Ti}$ precipitates. The formation of $\eta$-$\text{Ni}_3\text{Ti}$ precipitates consumes Ni from the matrix, which substantially inhibits the spinodal decomposition and refines the size of Cr-rich precipitates [16]. Plastic deformation of maraging steels also increases the density of $\eta$-$\text{Ni}_3\text{Ti}$ precipitates and promoted an earlier peak aging time and a higher peak hardness [19].

In most of the steels there are several types of precipitates, therefore their spatial distribution is complicated. Custom 465* (UNS S46500) is a martensitic age-hardenable stainless steel that contains only $\eta$-$\text{Ni}_3\text{Ti}$ precipitates, making it an ideal steel to study the interaction and orientation relations (ORs) between the precipitates. The $\eta$-$\text{Ni}_3\text{Ti}$ precipitate is known to have the shape of an elongated ellipsoid growing parallel to closed-packed directions and closed-packed planes of the matrix. Many observations [20–25] have shown arrays of precipitates parallel to the $\{111\}$ bcc directions, and recently the spatial distribution of $\eta$-$\text{Ni}_3\text{Ti}$ precipitates around the $\{111\}$ bcc in Custom 465* was measured by Rauch et al. [26]. Thus, the precipitates may form four intersecting arrays in space. TEM images appear to show random distribution of precipitates in each array. This calls for the following question which has not been answered before: Are there preferred relations between neighboring precipitates within an array and between intersecting arrays?

New particles formed in the initial stages of precipitation are coherent with the matrix. The coherent precipitates are associated with large elastic strains and energy. The tendency to reduce the elastic energy may influence the crystallographic structure, the shape and habit plane. For example, $\text{Ni}_3\text{Ti}$ precipitates have fcc crystallographic structure and spherical shape in A-286 austenitic steel [27], or a cubic shape in Ni-based superalloys [28]. Changing the matrix to bcc structure leads to hcp crystallographic structure that favors needle-shaped precipitates [13]. Elastic interactions with other defects, e.g., other particles, dislocations and even twins, provide other avenues for saving energy, thereby influencing the alloy’s properties [29–33]. Important interactions may set up among precipitates, giving rise to ORs between the precipitates; for example, $\text{Ni}_3\text{Ti}$ precipitates in A-286 steel have weak interaction [27], while in Ni-based superalloys they exhibit almost a perfect ordering [28,34–37]. Precipitates in Al and Mg alloys also show high degree of ordering [33,38–41]. The elastic fields and interaction in a static lattice have been solved analytically by Eschelby, Khachatryan, and Mura [54–56]. In the last decades, a new approach was applied to follow the development of microstructure in solids on large length and time scales [35,36,41]. These phase-field models define a mesoscopic free energy functional of the microstructure. At any time, the microstructure is represented by a set of continuous fields of the concentration and of long-range order parameters. The evolution of each field is obtained by solving a kinetic equation governed by its driving force. In this way, the evolution of the precipitate’s size, shape and distribution are obtained. The phase-field approach has been applied to follow the development of precipitates in Ni-based superalloys with dilatational misfit [42,43], their coarsening and ordering [42–45], order formation due to elastic interactions among several variants with tetragonal misfit [45–47], selection of one variant out of several variants [44], spindleal [48] and martensitic [47] transformations. The effect of elastic inhomogeneity on these phenomena has been found by iterative solution of the field equations [27,42].

In this study, the elastic fields generated by coherent $\eta$-$\text{Ni}_3\text{Ti}$ precipitates in the bcc matrix are calculated, the interaction energy between precipitates is deduced, and hence its effect on their ORs is evaluated. The conclusions are compared to TEM observations of Custom 465* in different aging conditions.

2. Experimental

Custom 465* stainless steel was purchased from Carpenter Technology (Wyoming, PA, USA). The chemical composition of the steel was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inert gas fusion (IGF) analyses, yielding 10.9 Ni, 10.7 Cr, 1.4 Ti, 0.86 Mo, 0.04 Al, 0.04 Zn, and 0.0046 C (wt%), the remaining being Fe. The 2-inch diameter rod was received in the solution annealed (SA) and cold-treated condition, and was characterized in the SA and aged conditions in previous studies [13,49,50]. The steel was aged for four hours at several temperatures, corresponding to the definition of aging treatments of Custom 465*: 482 ± 5 °C (H900), 510 ± 5 °C (H950), 538 ± 5 °C (H1000), 560 ± 5 °C (H1040), 593 ± 5 °C (H1100), 648 ± 5 °C (H1200). Characterization of the precipitates in these aging conditions is provided elsewhere [13].

Samples in the SA and aged conditions were examined by JEOL JEM-2100 F TEM. TEM specimen preparation consisted of mechanical polishing to a 30-µm thickness on a 1 000 grit SiC grinding paper, followed by mechanical polishing with 6 and 1 µm diamond pastes, using polishing cloths and water as lubricant. 3-mm diameter disks were cut using a punch, and the hole in the central area of the disk was ion-milled using a Gatan precision ion polishing system (PIPS) for electron transparency.

The ORs between the $\eta$-$\text{Ni}_3\text{Ti}$ precipitates and the martensite matrix were $(111)_{\text{m}}//[001]_{\text{Ni}_3\text{Ti}}$, and $(111)_{\text{m}}//[1120]_{\text{Ni}_3\text{Ti}}$, as calculated from Fig. 8a,b. As reported for Fe-20Ni-5Mn alloy [20,21,60], in the BF-TEM image (Fig. 4b) there are three variants of $\eta$-$\text{Ni}_3\text{Ti}$ precipitates at an angle of 60° from each other. A dark-field (DF) image taken at the (2240) $\eta$-$\text{Ni}_3\text{Ti}$ reflection, which is parallel to the long axis of one of the variants of precipitates, revealed a rod-shaped morphology. For each aging treatment, the diameters and lengths of precipitates were examined and measured from DF images obtained at an identical crystallographic orientation: the (2240) $\eta$-$\text{Ni}_3\text{Ti}$ reflection at [112]$_{\text{m}}$ zone axis of martensite.

3. Crystallographic analysis

In steels with lath martensite structure, TEM observations reveal rod-shaped $\eta$-$\text{Ni}_3\text{Ti}$ precipitates with their long axis being parallel to the $\{111\}$ directions in the matrix phase. The ORs between the hexagonal precipitates ($a = 0.5101$ nm, $c = 0.8307$ nm) [51] and the bcc lath martensite ($a = 2.878$ nm [52]) are: $(111)_{\text{m}}//(1120)_{\text{Ni}_3\text{Ti}}$, $(001)_{\text{m}}//[0001]_{\text{Ni}_3\text{Ti}}$.

There are several possible orientations to situate the dense planes and directions in the hexagonal second phase to lay parallel to the dense planes and directions in the bcc matrix, e.g. according to Pitsch-Schrader-P-S or Burgers [53]. Fig. 1 shows hexagonal groups of atoms in the precipitate (red hexagon) and in three bcc unit cells of the matrix (blue hexagon). Fig. 1a illustrates the P-S ORs in which the $<100>$ or $<110>$ directions are parallel to the $<210>$ or $<011>$ directions, respectively. In order to generate the Burgers relation between the hexagonal basal plane of $\eta$-$\text{Ni}_3\text{Ti}$ and the irregular hexagonal (110) plane of the bcc matrix [21,25,26,53], the $(2110)$ directions in the $\eta$-$\text{Ni}_3\text{Ti}$ have to be rotated by 5.26° relative to the nearest($111$) direction of the matrix, as shown in Fig. 1b. It turns out that if Burgers is associated with smaller mismatch both quantitatively and experimentally, this is the observed relation [21,25,26]. Fig. 8a,b shows selected area electron diffraction (SAED) micrographs supporting the actual ORs between the precipitates and the matrix.

The misfit strain calculated in the coordinate axes 
$x = [111]$, $y = [112]$, $z = [110]$ is:
\[
\begin{bmatrix}
0.02257 & -0.0904 & 0 \\
-0.0904 & 0.0606 & 0 \\
0 & 0 & 0.0198
\end{bmatrix}
\]

The misfit strain in the bcc coordinate system \((x' = [110], y' = [010], z' = [001])\) is found by the transformation equation of a second-rank tensor, \(\tilde{\varepsilon}_{ij} = a_{kk} a_{kl} \tilde{e}_{kl} \)

\[
\begin{bmatrix}
0.0499 & -0.0301 & 0.0064 \\
-0.0301 & 0.0499 & 0.0064 \\
0.0064 & 0.0064 & -0.1181
\end{bmatrix}
\] (2)

### 4. Calculation method

The displacements \(u_i(x)\) due to the homogeneous precipitate in Eq. (3) have been expressed as a Fourier series in \([54,55]\):

\[
u_i(x) = \sum_k \left( C_{ijmn}^k \eta_0 \Omega_{ik} \exp(i k \cdot x) \right)
\]

where summation should be taken over the reciprocal space vectors \(k, \Omega\) is the Fourier transform of the Green function defined by \(C_{ijmn}^k = \frac{1}{\Omega_{ik}} \Omega_{kj} \Omega_{mn}\), and \(C_{ijmn}^k\) are the transformation strains as defined in Eq. (2), and \((\cdot)\) is the shape function of the precipitate, defined as unity in the precipitate and zero in the matrix. We approximate the shape of the precipitate by an ellipsoid with an aspect ratio of \(1:3\) (Fig. 2). For the case of multi-particle system, the shape function of particles displaced from the origin, \(\theta(k)\), is conveniently calculated from the shape function of particles centered in the origin of coordinates \(\theta_0(k)\) by applying the Fourier displacement theorem:

\[
\theta(k, d) = \theta_0(k) \exp(-ik \cdot d)
\] (4)

The elastic strains are derived from the compatibility equation, and the stresses are related to the strains by Hooke’s law.

In order to calculate the total elastic energy in the system one has to integrate the products of elastic strains and stresses over the volume of the whole system, including the precipitates and matrix:

\[
E_{el} = \frac{1}{2} \int_{V} \sigma_{ij} \varepsilon_{ij} dV = \frac{1}{2} \int_{V} \sigma_{ij} \tilde{e}_{ij}^T dV
\] (5)

Eshelby [56] proved that the total elastic energy can be expressed as an integral only over the volume of the precipitate alone, as expressed by the last term in Eq. (5). He also proved that the interaction energy between two precipitates can be calculated as an integral of the stresses produced by one precipitate A over the volume of the neighboring particle B:

\[
E_{int} = -\frac{1}{2} \int_{V} \sigma_{ij} \varepsilon_{ij} \theta(r) dV
\] (6)

According to Parsa’s theorem, the integral over the whole space of a product of functions in the real space is equal to the integral on their Fourier transforms over the whole reciprocal space

\[
E_{int}(d) = -\frac{1}{2} \int \sigma_{ij}(r) \varepsilon_{ij} \theta(r) d^3k = -\frac{1}{2} \int \sigma_{ij}(k) \varepsilon_{ij} \theta(k) \exp(-ik \cdot d) d^3k
\] (7)

This equation, first written by Khachaturyan [55], makes it possible to obtain the interaction energy of particle A with particles B located at any point \(d\) in the space around particle A by a single application of the Fast Fourier Transform (FFT) algorithm. All the sums in the present work were calculated employing this algorithm with 256\(^3\) terms. The elastic constants representing the bcc matrix were taken as the constants of pure \(\alpha\)-iron [57]: \(C_{11} = 232\) GPa, \(C_{12} = 136\) GPa, \(C_{44} = 117\) GPa.

In order to apply the analytic solution for several precipitates one has to assume homogeneous system, namely that the elastic constants of the precipitates and the matrix are equal. Ordinarily, there is a small variation in the elastic constants among metals, and estimations of the variation in energy due to the assumption of homogeneity show that it introduces only small differences [58,59]. The homogeneity assumption also allows the use of linear superposition of several precipitates [56].

### 5. Results and discussion

#### 5.1. The preferred shape and the self-energy

Fig. 2a describes the calculated elastic energy in \(\eta\)-\(\text{Ni}_3\text{Ti}\) precipitates in the matrix as a function of the shape of the precipitate. The assumed shapes are ellipsoids of revolution with \(a = c = b\); thus, the shape of the precipitate varies from a disk shape, through a sphere (\(b/a = 1\)) to a needle shape as the aspect ratio \(b/a\) increases (the black curve). The results predict that the \(\eta\)-\(\text{Ni}_3\text{Ti}\) precipitates will favor an ellipsoid-shaped morphology with a high aspect ratio. Experimentally, needle-shaped precipitates with about \(b/a = 3\) (Fig. 2b), are observed in Custom 465\(^*\) in the peak-aged conditions (H900 and H950); they are characterized by maximal values of hardness [13]. As the precipitates lose their coherency due to overaging (Fig. 2c), their aspect ratio increases up to \(b/a = 5\) at a temperature of 648°C (H1200). At this stage, the effect of the elastic energy reduces, and the contribution of the surface energy is minor,
therefore one may assume that anisotropic interface mobility is responsible to the elongated shape.

Fig. 3 describes strain maps of the resulting equilibrium between a $\eta$-Ni$_3$Ti precipitate and the bcc matrix. Fig. 3a presents the $\varepsilon_{xx}$ in the X-Y plane, while Fig. 3b,c describes the $\varepsilon_{yy}$ and $\varepsilon_{zz}$ strains, respectively, in the dense (110) plane. The effects of the strains are of short range and give rise to compressive radial stresses and to tensile tangential stresses in the matrix.

5.2. The elastic interaction between $\eta$-Ni$_3$Ti precipitates

TEM observations show that precipitates grow such that their close-packed planes and directions are parallel to the close-packed planes and directions in the matrix. There are four equivalent $<111>$ directions in the bcc lattice (Fig. 4a). The angle between each pair of $<111>$ directions is 109.5° (or 70.5°). Fig. 4b is a bright-field (BF) TEM image of $\eta$-Ni$_3$Ti precipitates, demonstrating three out of four different orientations after H1000 aging treatment.

The crystallographic orientation of a precipitate parallel to a certain $<111>$ direction is, however, not unique since the close-packed plane may lie parallel to one out of three (110)$_{bcc}$ planes of the matrix that contain the same $<111>$ axis. In each variant, one principal strain is parallel to the $<111>$ axis, the second is normal to the same axis in the same plane, and the third is normal to the habit plane. The principal strains are common in all variants; they differ only by the orientation of these strains. Fig. 4c illustrates three possible habit planes available for a precipitate laying parallel to the [111] axis and the three possible habit planes available for a second precipitate laying parallel to the [111] axis, along with the transformation strains (in the x,y,z axes) associated with each orientation.

Therefore, there are 12 crystallographic variants of single precipitates, and 144 possible orientation variants of pairs of precipitates (see Appendix). Careful examination of these variants reveal that they may be classified into five groups of crystallographically independent pairs of precipitates, illustrated in Figs. 5–7. Table 1 describes each crystallographic group and the maximum value of the elastic interaction between each pair. The highest interaction energy is obtained for pairs of parallel, co-axial precipitates with habit planes intersected at 60°. Lower values are obtained for parallel pairs of co-axial precipitates laying on the same habit plane, or pairs of precipitates laying along intersecting axes with habit planes intersecting at 60°. The remaining orientations
have interaction energy three times smaller than the maximal interaction.

The self-energy of two η–Ni₃Ti precipitates is about 1.2 GJ/m$^2$ and the interaction energy of parallel precipitates reaches ~7% of the self-energy in OR (a), and ~5% of the self-energy in ORs (b) and (c). The typical order of magnitude of interaction energy that gives rise to exemplary ORs of precipitates in Ni-based superalloys along the three <100> axes is about 5% of the self-energy that is lower by an order of magnitude than self-energy in Custom 465® [34,35]. Here, the ORs are expected to occur in a more sophisticated manner along the four <111> axes (Fig. 4a), and this is probably the reason that these ORs between the precipitates have not been described in earlier studies.

In Figs. 5–7, representative maps of the interaction energies in the three combinations with highest interaction energies are shown. Each map describes the interaction between a precipitate located at [-0.7,0,0] length units behind the center of the map, and a second precipitate surrounds it (see calculation method in Section 4). Three types of sites are found: (a) energy minima, where attractive interactions are obtained when stresses generated by one precipitate overlap with stresses with the opposite sign generated by a neighboring precipitate; (b) energy maxima, where the repulsive interactions are obtained when stresses generated by one precipitate overlap with stresses with the same sign generated by a neighboring precipitate; (c) between the energy extrema are regions of relative indifference.

Figs. 5a and 6a illustrate the interaction energy maps in the (110) plane between two parallel η–Ni₃Ti precipitates with equal size, exhibiting the highest interaction. The first case represents precipitates lying on habit planes inclined at 60°, whereas the second case is associated with two parallel precipitates with the same habit planes (see Table 1, ORs (a) and (b)). In both cases, the highest interaction is found when the precipitates are in proximity, displaced by approximately two radii between each other. The centers of interacting precipitates are slightly diverted from each other, located side-by-side in OR (a) or head-to-tail in OR (b). Figs. 5b and 6b show maps of the $\epsilon_{xx}$ strain in the (110) plane of two parallel η–Ni₃Ti precipitates located in the respective highest interaction configurations. Both figures illustrate the overlap between strains set up in the matrix due to the misfitting precipitates. The strains in Fig. 5b are different in the two precipitates since their habit planes are different, while the strains in Fig. 6b are similar since the habit planes are parallel. Fig. 5c,d are real BF and DF TEM images of needle-shaped η–Ni₃Ti precipitates with side-by-side or head-to-tail relations at almost touching proximity of parallel precipitates that is very similar to the configurations predicted by the maps of interaction energy. The DF image in Fig. 5d reveals that some of the precipitates vanished since they are laying parallel to a different habit plane while others sustain since the co-axial precipitates lay on parallel habit planes.

Fig. 7a presents the interaction energy map on the (110) plane of two precipitates inclined at 109.5° (or 70.5°) to each other since their long axes are parallel to different <111> axes and habit planes intersecting by 60° (OR (c)). Fig. 7b describes the map of the $\epsilon_{xx}$ strain on the (110) plane of two parallel η–Ni₃Ti precipitates with 1:3 aspect ratio positioned at the highest interaction configuration. As in the case of precipitates that are parallel to each other, the favored relation is observed when the precipitates are almost in touching each other. Fig. 7c,d shows TEM images of η–Ni₃Ti precipitates. The images conform with the orientation of 109.5° between the precipitates that was expected from their relation to the <111> axes. Notably, precipitates with touching proximity are commonly observed, in line with the calculations presented as energy maps (Fig. 7a). Moreover, The DF image in Fig. 7d demonstrate that only one of the needle-shaped η–Ni₃Ti precipitates can be seen, implying that the precipitates are laying in different habit planes conforming with OR (c) and OR (e). Since the multiplicity and the interaction energy of OR(c) is significantly higher than those of OR (e), it is most probable that the image represents OR(c).

It is possible that the precipitates that appear adjacent to each other in TEM images lie far below each other in the real space. Indeed, it is expected that the precipitates laying on different <111> axes will be inclined at 109°, but their frequent proximity indicates that this is an outcome of interaction between the precipitates. The same alloy was carefully studied by TEM by Rauch and Veron [26]. In their study, many proximate pairs of parallel and 109°-inclined precipitates were observed. Direct support of our assumptions was provided by APT studies [15,17,19] of η–Ni₃Ti precipitates in lath martensite maraging steels, exhibiting relatively large abundance of the said ORs.

How these tendencies combine in the real three-dimensional (3D) arrangement of many precipitates is difficult to grasp. The arrangement along the dense <111> orientations and (110) planes is evident in the TEM observations (Fig. 8). TEM DF images illustrate clusters of parallel precipitates along the different <111> orientations (Fig. 8c,d). This is clear since the self-elastic energy of each precipitate is determined by the best fitting of closed-packed orientations (Fig. 8a,b). The interaction between different branches is not obvious experimentally in Custom 465® stainless steel, as demonstrated by the TEM BF images in Fig. 8e,f, due to four reasons: (a) the low volume fraction (6 vol%) of precipitates hinders the occupation of all the favored sites; (b) the interaction energies are
Fig. 4. (a) The four <111> directions in space. (b) TEM BF taken at zone axis [112], image of η-Ni₃Ti precipitates along three different axes in the H1000 condition. (c) Two representatives <111> axes and the three possible habit planes along each axis, along with the transformation strains, in the xyz coordinate system, associated with each orientation. These strains are obtained by the proper transformations of Eq. (2).
Fig. 5. (a) The interaction energy map on the (110) plane between two parallel \( \eta \)-Ni\(_3\)Ti precipitates with equal size laying on habit planes inclined at 60°. (b) A map of the \( \varepsilon_{xx} \) strain generated by the two precipitates positioned in the highest interaction configuration in (a). (c) TEM BF image taken at zone axis \([112]_p\) of \( \eta \)-Ni\(_3\)Ti precipitates in the H1100 condition. The white and the blue arrows point at parallel precipitates. (d) DF image from the \( (22\bar{4}0) \) reflection of one variant of the \( \eta \)-Ni\(_3\)Ti precipitates. Marked by blue arrows are precipitates that vanish since they are laying parallel to different habit planes, while precipitates with parallel habit planes remain visible and marked by white arrows. Adapted from Fig. 3 in Ref. [13], with permission from Elsevier.
Table 1 F
Five groups of crystallographically independent pairs of precipitates classified by the orientation relation (OR), the number of pairs in each OR, and the elastic interaction between them per unit volume of the precipitates.

<table>
<thead>
<tr>
<th>Orientation Relation (OR)</th>
<th>No. of pairs</th>
<th>$E_{int}$ (MJ/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Co-axial precipitates with habit planes intersecting at 60°</td>
<td>24</td>
<td>-87.5</td>
</tr>
<tr>
<td>(b) Co-axial precipitates with parallel habit planes</td>
<td>12</td>
<td>-60</td>
</tr>
<tr>
<td>(c) Precipitates laying along intersecting axes, with habit planes intersecting at 60°</td>
<td>72</td>
<td>-62</td>
</tr>
<tr>
<td>(d) Precipitates laying along intersecting axes, with parallel habit planes</td>
<td>12</td>
<td>-33</td>
</tr>
<tr>
<td>(e) Precipitates laying along intersecting axes, with habit planes intersecting at 90°</td>
<td>24</td>
<td>-28</td>
</tr>
</tbody>
</table>

Fig. 6. (a) The interaction energy maps on the (110) plane between two parallel $\eta$-Ni$_3$Ti precipitates with the same habit planes. (b) Map of the $\varepsilon_{xx}$ strain in the (110) plane of two parallel $\eta$-Ni$_3$Ti precipitates located at the highest interaction configuration.
Fig. 7. (a) Interaction energy map on the (110) plane of two precipitates inclined at 109.5° (or 70.5°) to each other and habit planes intersecting by 60°. (b) A map of the $\varepsilon_{xx}$ strain generated by the two precipitates positioned in the highest interaction configuration in (a). (c) TEM BF image taken at zone axis [112] of $\eta$-Ni$_3$Ti precipitates in the H1150 aging condition, showing two precipitates inclined at 109.5° and another pair inclined at 70.5°. (d) DF image from the (2240) reflection of one variant of the $\eta$-Ni$_3$Ti precipitates. The figure reveals that some of the precipitates vanish since they are laying in different habit planes.

Adapted from Fig. 3 in Ref. [13], with permission from Elsevier.
much lower than the self-elastic energy; (c) the observation conditions in the TEM hinders the simultaneous observation of all the existing orientations; (d) the precipitates are arranged along four axes in a 3D space. The interaction energy in the Custom 465® steel is larger than that in Ni-based superalloys in absolute magnitude, yet ordering in the steel is not obvious as in superalloys. The main reason for the lack of clear ordering is most likely the low volume fraction of precipitates. Experimentally, the precipitates often appear in dense clouds surrounded by less populated regions (Fig. 8c,d). These clouds may indicate preferred nucleation around some primary precipitates. In this study, evidence is provided that effective interactions exist inside branches and between interpenetrating branches, as observed in Figs. 5c,d and 7c,d.

6. Conclusions

The effect of the elastic energy on the shape and orientation relations (ORs) between \( \eta \)-Ni\(_3\)Ti precipitates in lath martensite was studied using the quasi-analytic Fourier transform method and TEM observations of Custom 465® stainless steel. Since the precipitates are growing in arrays parallel to the four closed-packed axes, \( <111> \)\(_{\text{bcc}}\), and closed-packed planes, \( (110)_{\text{bcc}} \), of the matrix, there are 144
possible orientation-pairs, which are classified herein into five groups of crystallographically independent pairs. Accordingly, the elastic interaction energy within each group was calculated. The following conclusions were drawn:

1. The η-Ni$_3$Ti precipitates favor an ellipsoidal shape with a high aspect ratio. Experimentally, needle-shaped precipitates with ca. b/a = 3 are observed in Custom 465® in the peak-aged condition.

2. The interaction energy of two precipitates reaches up to ~7% of the self-energy, higher than the typical interaction energy of precipitates in Ni-based superalloys. In steels, the ORs between the precipitates are expected to occur in a more sophisticated manner along the four <111> axes.

3. The top three orientation relations that represent the highest interactions are when the precipitates are parallel to each other or when they are laying along intersecting axes with habit planes intersecting at 60°. In those orientation relations, the highest interaction is found when two precipitates touch each other and are positioned either side-by-side or head-to-tail. These predictions are in good agreement with TEM observations of individual pairs.

4. The precipitates often appear in dense clouds surrounded by less populated regions. These clouds may indicate preferred nucleation around some primary precipitates that interact with the others. However, the low volume fraction of precipitates (6 vol%) in Custom 465® hinders the occupation of all of the favored sites, and the observation conditions in the TEM makes it difficult to observe simultaneously all of the existing orientations. It is noteworthy that uneven density of precipitates gives rise to non-homogeneous mechanical properties on the microscopic scale.

**CRediT authorship contribution statement**

**M. Shmulevitsh:** Conceptualization, Data curation, Investigation, Validation, Visualization, Writing – original draft. **S. Ifergane:** Data curation, Investigation, Visualization, Writing – review & editing. **N. Eliaz:** Funding acquisition, Supervision, Visualization, Writing – review & editing. **R. Shneck:** Conceptualization, Supervision, Writing – original draft.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Appendix**

The 144 combinations of crystallographically independent pairs of precipitates, classified according to the orientation relations (ORs) between the dense axes and the dense planes in the bcc matrix, 1: co-axial precipitates with parallel habit planes, 2: co-axial precipitates with habit planes intersecting by 60°, 3: precipitates lying along intersecting axes with parallel habit planes, 4: precipitates lying along intersecting axes with habit planes intersecting by 90°.

| [111], (110) | [111], (110) | [111], (110) | [111], (110) | [111], (110) | [111], (110) | [111], (110) | [111], (110) | [111], (110) | [111], (110) | [111], (110) | [111], (110) | [111], (110) | [111], (110) | [111], (110) |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| [111], (110) | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 | 1 2 3 4 4 |
| [111], (110) | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 | 2 3 4 5 4 |
| [111], (110) | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 | 3 4 5 6 5 |
| [111], (110) | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 | 4 5 6 7 6 |
| [111], (110) | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 | 5 6 7 8 7 |

**References**


