

1 **Synergistic alloying effects on nanoscale precipitation and mechanical properties of**
2 **ultrahigh-strength steels strengthened by Ni₃Ti, Mo-enriched, and Cr-rich**
3 **co-precipitates**

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15 **Abstract:**

16 The synergistic effects of Mo, Ti, and Cr on nanoscale precipitation and mechanical
17 properties of maraging stainless steels were systematically studied using high-resolution
18 scanning transmission electron microscopy, atom probe tomography (APT), thermodynamic
19 and first-principles calculations, and mechanical tests. Our results reveal a notable
20 precipitation pathway involving the co-precipitation of Ni₃Ti, Mo-enriched, and Cr-rich
21 precipitates; their formations are not separated, but rather highly interacted. The APT results
22 indicate that Mo partitions to the Ni₃Ti precipitate core in the early stage of precipitation,
23 which doubles the number density of Ni₃Ti precipitates. Our calculations indicate that the Mo

1 partitioning not only increases the chemical driving force, but also reduces the strain energy
2 for nucleation, thereby accelerating Ni₃Ti precipitation. As the precipitation proceeds, Mo
3 atoms are rejected from the Ni₃Ti precipitate core to the interface between the Ni₃Ti
4 precipitates and matrix, which leads to the heterogeneous nucleation of Mo-enriched
5 precipitates on the outer surface of the Ni₃Ti precipitates. This results in a substantial size
6 refinement of Mo-enriched precipitates. In addition, the formation of Ni₃Ti precipitates
7 consumes Ni from the matrix, which substantially inhibits the spinodal decomposition and
8 refines the size of Cr-rich precipitates. The cooperative strengthening of Ni₃Ti, Mo-enriched,
9 and Cr-rich co-precipitates leads to the development of new steels with a strength of 1.8 GPa;
10 the contributions of these precipitates to the strengthening were quantitatively evaluated in
11 terms of precipitate shearing and Orowan dislocation looping mechanisms.

12 **Keywords:** maraging steel, precipitation, microstructure evolution, mechanical property

13 **1. Introduction**

14 Ultrahigh-strength steels generally refer to structural steels with a yield strength of more
15 than 1380 MPa (200 ksi) [1]. They are widely used in the aerospace industry because they
16 allow for the design of light-weight, cost-effective, and energy-efficient components [1-3].
17 Maraging steels are an important class of ultrahigh-strength steels that can be hardened by the
18 precipitation of intermetallic nanoprecipitates at intermediate temperatures [4,5]. This class of
19 steels exhibits ultrahigh strength, high ductility, and high toughness, rendering them useful in
20 many applications such as rocket engine casings, submarine hulls, and cryogenic missiles
21 [6,7]. Conventional maraging steels, however, have two major disadvantages: high cost due

1 to the high Co and Ni contents and poor corrosion resistance due to the absence of Cr [8-10].
2 A viable solution to the first problem is to reduce the Ni and Co contents while optimizing the
3 Ti and Mo concentrations; this would allow for the development of new maraging steels with
4 comparable mechanical properties to those of conventional maraging steels at a substantially
5 lower cost. As for the second problem, the addition of Cr to maraging steels improves their
6 resistance to corrosion and oxidation, allowing them to withstand harsh conditions, such as
7 elevated temperatures [11,12]. It is noticed that the significant changes in alloy composition
8 cause a large variation in the precipitate microstructure, including in the type and morphology
9 of precipitates as well as their interactions [13-16]. These factors significantly affect the
10 degree of precipitation strengthening and consequently the mechanical properties of the
11 steels.

12 For example, Mo-enriched precipitates can precipitate in different forms, such as the
13 Fe₂Mo-type Laves phase, Fe₇Mo₂-type ω phase, Fe₇Mo₆-type μ phase, trigonal R phase, and
14 quasicrystalline R' phase, depending on the alloy composition and processing variables
15 [17-20]. Sha et al. reported that Ti is more active than Mo in the early stage of precipitation
16 and that the precipitation behavior of Mo is modified owing to the presence of Ti, especially
17 when aging at low temperatures [21]. Tian et al. found that with optimized compositions,
18 Ni₃Ti and Mo-enriched precipitates form a core-shell structure, which plays a crucial role in
19 the precipitation strengthening, leading to the development of new steels with a strength of
20 1.9 GPa and decent ductility [22]. The precipitation of Cr-rich phases was observed in
21 Cr-containing maraging steels after long-term aging. Thuvander et al. reported that

1 η -Ni₃(Ti,Al) and Cr-rich α' phases form co-precipitates in contact with each other during
2 aging at 475 °C [23]. These studies suggest that the formation of different types of
3 precipitates in maraging stainless steels may not be separated; there might exist some
4 interactions among different types of precipitates. However, a clear picture of the
5 precipitation pathway and nanostructure evolution of these materials remains elusive. In
6 particular, an atomic-scale understanding of precipitate chemistry and solute partitioning of
7 maraging stainless steels is still lacking, and it is still an open question how the individual
8 and/or synergistic effects of precipitate-forming elements on the precipitate chemistry, solute
9 partitioning, and precipitation pathways in these materials. To date the key factors governing
10 the nucleation mechanism and evolution pathways of Ni₃Ti, Mo-enriched, and Cr-rich
11 precipitates in maraging stainless steels have not been well characterized, and the relationship
12 between the precipitate microstructure and mechanical properties of these materials has not
13 yet been established. Thus, elucidating the correlations among the alloying elements,
14 nanoscale co-precipitation, and strengthening effects in maraging stainless steels is of
15 practical importance.

16 In this study, we aim to understand the synergistic alloying effects and nanoscale
17 co-precipitation mechanisms of maraging stainless steels as well as understand the correlation
18 between the precipitate microstructure and mechanical properties of these materials.
19 Specifically, the synergistic effects of Mo, Ti, and Cr on the precipitation behavior and
20 mechanical properties of three model steels, i.e., Ti-alloyed, Mo-alloyed, and Ti/Mo-alloyed
21 steels, were systematically studied through high-resolution transmission electron microscopy

1 (HR-TEM), high-angle annular dark field scanning TEM (HAADF-STEM), atom probe
2 tomography (APT), thermodynamic and first-principles calculations, and mechanical tests.
3 Particular effort was made to understand the nucleation mechanism and cooperative evolution
4 of nanoscale Ni₃Ti (η phase), Mo-enriched (ω phase), and Cr-rich (α' phase) co-precipitates in
5 maraging stainless steels.

6 **2. Experimental**

7 The three steels with different Ti and Mo contents were prepared by vacuum induction
8 melting and cast into ingots of 25 kg. Chemical compositions (wt.%) of the steels measured
9 by chemical analysis are given in Table 1. For simplicity, these steels are hereafter referred to
10 as Ti-steel, Mo-steel, and Ti/Mo-steel. The as-cast ingots were homogenized for 20 h at
11 1250 °C and hot-forged into square bars with a cross section of 40 × 40 mm², followed by air
12 cooling. The forged bars were solutionized for 1 h at 1050 °C and immersed in liquid
13 nitrogen for 1 h and then aged at 500 °C for various periods of time.

14 Mechanical properties were determined by Rockwell hardness, fracture toughness, and
15 tensile tests at room and elevated temperatures. Room-temperature hardness measurements
16 were conducted under a load of 150 kg and a dwell time of 5 s. For each sample, at least five
17 indents were made on polished surfaces, and the average values were reported. Rod tensile
18 samples with a gauge diameter of 5 mm and a gauge length of 25 mm were prepared by
19 electrodischarge machining. Room-temperature tensile tests were conducted on a MTS810
20 testing machine at a strain rate of $2 \times 10^{-3} \text{ s}^{-1}$. Elevated-temperature tensile tests were
21 conducted on a SUST testing machine at a strain rate of 10^{-3} s^{-1} . Fracture toughness tests were

1 performed according to ASTM E399 standard testing procedure using compact tension
2 specimens.

3 Scanning electron microscopy (SEM) was carried out on specimens etched with Vilella's
4 reagent and using FEI INSPECT SEM operated at 20 kV. TEM observations and selected
5 area electron diffraction (SAED) were conducted using a JEM 2100F microscope operated at
6 200 kV. HAADF-STEM observations were carried out on an aberration-corrected Titan G2
7 60-300 microscope operated at 300 kV. Thin TEM/STEM foils were prepared by grinding
8 3-mm-diameter discs to a thickness of 50 μm and then jet electro-polished using a Struers
9 TenuPol-5 polisher in a solution consisting of 10 vol.% HClO_4 and 90 vol.% $\text{C}_2\text{H}_5\text{OH}$ at
10 $-20\text{ }^\circ\text{C}$. APT experiments were performed in a LEAPTM 5000XR in voltage mode. Data
11 acquisition was performed at a temperature of 60 K, a pulse repetition rate of 200 kHz, a
12 pulse fraction of 20%, and an ion collection rate of 0.3% ions per field evaporation pulse. The
13 Imago Visualization and Analysis Software (IVAS) 3.8 was used for three-dimensional
14 reconstructions, composition analyses, and the creation of isoconcentration surfaces.

15 Phase fractions and elemental compositions in thermodynamic equilibrium were
16 calculated using the software Thermo-Calc 3.0.1, together with an Fe-based database
17 (TCFE7). First-principles calculations were performed using the Vienna Ab initio Simulation
18 Package (VASP) [24] with the projector augmented wave (PAW) method [25,26] for the
19 description of ions-electrons interaction and the Perdew-Becke-Erzenhof
20 exchange-correlation functional [27]. The cut-off energy of the plane wave basis set was
21 fixed at 350 eV. The gamma-centered k-point mesh was set to be $12 \times 12 \times 12$ for the 2-atom

1 body-centered cubic (BCC) Fe unit cell, and $6 \times 6 \times 4$ for the 16-atom Ni_3Ti , $\text{Ni}_3\text{Ti}_{0.75}\text{Mo}_{0.25}$,
2 and $\text{Ni}_3\text{Ti}_{0.5}\text{Mo}_{0.5}$ supercells. All structures were fully relaxed to a convergence of the total
3 energy of 10^{-6} eV and a residual force of 0.3 meV per atom. The Gaussian smearing of 0.1
4 eV was adopted for the electronic occupancy. The Ti3p4s3d, Fe3p4s3d, Ni3p4s3d, and
5 Mo4p5s4d were treated as valence states for all calculations. Spin polarized calculations were
6 performed for BCC-Fe due to its ferromagnetism.

7 **3. Results**

8 *3.1. Mechanical properties*

9 The Rockwell hardnesses of the Mo-, Ti-, and Ti/Mo-steels are shown in Fig. 1a as a
10 function of aging time at 500 °C. In the as-quenched state, the three steels have similar
11 hardness values (24–26 HRC). After aging for 0.5 h, the hardness of the Mo-steel increases to
12 32.8 ± 0.1 HRC and reaches a peak value of 44.5 ± 0.2 HRC after aging for 90 h. A further
13 increases in aging time results in a decrease in the hardness, indicating an overaging effect.
14 The hardness of the Ti-steel increases rapidly to 38.0 ± 0.3 HRC after aging for 0.5 h and to a
15 peak value of 47.8 ± 0.3 HRC after aging for 24 h, demonstrating a higher rate of age
16 hardening than the Mo-steel. The Ti/Mo-steel exhibits an even higher rate of age hardening
17 than the Ti- and Mo-steels, achieving a hardness of 43.1 ± 0.9 HRC after aging for 0.5 h.
18 Moreover, the Ti/Mo-steel attains a peak hardness of 52.4 ± 0.6 HRC after aging for 60 h,
19 which is considerably higher than the peak hardness of the Ti- and Mo-steels (44.5 ± 0.2 and
20 47.8 ± 0.3 HRC, respectively). Thus, the combination of Ti and Mo increases both the rate of

1 age hardening and the peak hardness, demonstrating a synergistic alloying effect on the age
2 hardening response of the steels.

3 Room- and elevated-temperature tensile tests were performed to further investigate the
4 synergistic effects of Ti and Mo on the mechanical properties of the steels. The
5 room-temperature engineering stress–strain curves of the three steels in the as-quenched and
6 peak-aged conditions are displayed in Fig. 1b, and the yield strength (YS), ultimate tensile
7 strength (UTS), elongation-to-failure (EL), and reduction in area (RA) are summarized in
8 Table 2. The Mo-, Ti-, and Ti/Mo-steels exhibit similar tensile properties in the as-quenched
9 state, with yield strengths of 663, 655, and 739 MPa, respectively, and ultimate tensile
10 strengths of 834, 836, and 905 MPa, respectively. After the peak-aging treatment the three
11 steels exhibit significantly different tensile properties. The Mo- and Ti-steels exhibit a
12 moderate increase in yield strength, increasing from 663 ± 12 MPa in the as-quenched state to
13 1274 ± 15 MPa in the 60-h aged state and from 655 ± 8 MPa in the as-quenched state to 1320
14 ± 13 MPa in the 24-h aged state, respectively. By contrast, the yield strength of the
15 Ti/Mo-steel increases from 739 ± 8 MPa in the as-quenched state to 1732 ± 15 MPa in the
16 60-h aged state, which is an increase of approximately 1000 MPa. Along with the increase in
17 yield strength, a slight reduction in the elongation-to-failure was noted; however, the steel is
18 still ductile, with an elongation-to-failure of $10.8\% \pm 2.0\%$ and a reduction in area of $45\% \pm$
19 4% . The room-temperature fracture toughness of the Ti-, Mo-, and Ti/Mo-steels in the
20 peak-aged condition are 24 ± 4 , 95 ± 7 , and 89 ± 5 MPa·m^{1/2}, respectively, which are
21 comparable to that of conventional maraging steels [28]. In addition, the tensile properties of

1 the three steels in the peak-aged conditions were tested at 400, 500, and 600 °C. The
2 representative stress–strain curves at 500 °C are shown in Fig. 1c, and the yield strengths of
3 the three steels are plotted in Fig. 1d as a function of testing temperature. The yield strengths
4 of the three steels decrease as the testing temperature increases, and the Ti/Mo-steel exhibits a
5 much higher yield strength than the Mo- and Ti-steels at all the testing temperatures. In
6 particular, the Ti/Mo-steel has a yield strength of over 1100 MPa at 500 °C, demonstrating a
7 high strength over a wide temperature range.

8 *3.2 Microstructure*

9 The microstructures of the Ti-, Mo-, and Ti/Mo-steels in the peak-aged conditions are
10 shown in the Supplementary Fig. S1. SEM images indicate that the three steels have a typical
11 tempered martensite structure with a prior-austenite grain size of approximately 50 μm and
12 no coarse precipitates. No significant differences in the micrometer-scale structure were
13 observed among the three steels. In the following section, we characterize the microstructure
14 of the three steels at the atomic- and nano-scale.

15 *3.3 Nanoscale precipitation*

16 *3.3.1 Ni₃Ti precipitates*

17 Figure 2 shows the bright-field TEM images of the Ti- and Ti/Mo-steels after aging for
18 0.5, 24, and 60 h at 500 °C. After the 0.5-h aging, no precipitates were observed in both the
19 Ti- and Ti/Mo-steels, possibly because of the extremely small size of the precipitates. As the
20 aging time increases, a high number density of rod-like precipitates (blue arrows) was

1 observed (Fig. 2c–f). These precipitates are typically less than 20 nm in length and 10 nm in
2 width. The HAADF-STEM images of the Ti- and Ti/Mo-steels after aging for 60 h are
3 displayed in Fig. 3a and b, respectively, where the electron beam is parallel to the $[011]_{\alpha}$
4 direction. The precipitates exhibit a rod-like morphology with a length of approximately 15
5 nm and a width of approximately 5 nm. The fast Fourier transformed (FFT) patterns (Fig. 3c
6 and d) reveal that the precipitates in both steels have a DO_{24} -ordered structure, which
7 corresponds to a Ni_3Ti -type η phase. The orientation relationship between the martensitic
8 matrix and η phase is that of Burgers, i.e., $\{110\}_{\alpha} // \{0001\}_{\eta}$ and $\langle 111 \rangle_{\alpha} // \langle 1\bar{1}20 \rangle_{\eta}$, which is in
9 agreement with data reported in the literature [29].

10 To explore the Mo effects on the composition and microstructure of Ni_3Ti precipitates,
11 we performed APT analyses on the Ti- and Ti/Mo-steels. The isosurfaces of 4 at.% Ti
12 concentration were used to visualize Ni_3Ti precipitates. The distribution of Ni_3Ti precipitates
13 in the Ti- and Ti/Mo-steels after aging for 0.5, 24 and 60 h is displayed in Fig. 4a–f, and their
14 number density and volume fraction are shown in Fig. 4g and h, respectively, as a function of
15 aging time. High number densities of near-spheroidal Ni_3Ti precipitates were observed in the
16 0.5-h aged specimens; the precipitates coarsen and change to a rod-like shape as the aging
17 time increases. The number density of Ni_3Ti precipitates in the Ti-steel increases from
18 approximately $9.0 \times 10^{23} \text{ m}^{-3}$ at 0.5 h to approximately $1.2 \times 10^{24} \text{ m}^{-3}$ at 24 h and then
19 decreases to approximately $6.0 \times 10^{23} \text{ m}^{-3}$ at 60 h, whereas that in the Ti/Mo-steel decreases
20 monotonically with aging time, from $2.4 \times 10^{24} \text{ m}^{-3}$ at 0.5 h to $1.2 \times 10^{24} \text{ m}^{-3}$ at 60 h. The
21 volume fraction of Ni_3Ti precipitates in the Ti-steel increases from 0.1% at 0.5 h to 3.7% at

1 60 h, whereas that in the Ti/Mo-steel increases from 0.5% at 0.5 h to 4.7% at 60 h. The
2 number densities and volume fractions of Ni₃Ti precipitates in the Ti/Mo-steel are higher than
3 those in the Ti-steel in all the conditions studied, indicating that the addition of Mo promotes
4 the Ni₃Ti precipitation in the Ti/Mo-steel.

5 The proximity histograms of the Ni₃Ti precipitates in the Ti- and Ti/Mo-steels after
6 aging for 0.5, 24, and 60 h are illustrated in Fig. 5, and the compositions of Ni₃Ti precipitate
7 cores are listed in Table 3. In the Ti-steel, the concentrations of Ni and Ti in the Ni₃Ti
8 precipitates increase with aging time, and the precipitate composition approaches the
9 equilibrium value of stoichiometric Ni₃Ti after aging for 60 h. In the Ti/Mo-steel, a local
10 enrichment of Ni and Ti in the nanosized Ni₃Ti precipitates is evident. Notably, and
11 potentially important for understanding the way in which Ni₃Ti precipitates are formed in
12 maraging steels, a strong partitioning of Mo to the Ni₃Ti precipitates was observed in the
13 early stage of precipitation in the Ti/Mo-steel. The Mo concentration in the precipitate core
14 decreases slightly from 4 at.% at 0.5 h to 3 at.% at 60 h, whereas the Mo concentration at the
15 precipitate/matrix interface increases from 2 at.% at 0.5 h to 3 at.% at 24 h and to 3.5 at.% at
16 60 h.

17 3.3.2 *Mo-enriched precipitates*

18 Figure 6a–c shows the Mo atom distribution in the Ti/Mo-steel in the 0.5-h, 24-h, and
19 60-h aged conditions, respectively. A uniform distribution of Mo atoms was observed in the
20 0.5-h aged condition, whereas a clear Mo segregation was detected in the 24-h and 60-h aged
21 conditions. 6 at.% Mo isoconcentration surfaces were used to depict the Mo-enriched

1 precipitates in the 24-h and 60-h aged conditions (Fig. 6d and e, respectively); the Ni₃Ti
2 precipitates are included to indicate the relative position of the Mo-enriched and Ni₃Ti
3 precipitates. Notably, almost all the Mo-enriched precipitates are in contact with the Ni₃Ti
4 precipitates. To further understand how Ni₃Ti affects the formation of Mo-enriched
5 precipitates, the evolution of solute partitioning was carefully examined at the atomic- and
6 nano-scale. 1-nm-thick atom maps through the centers of the Ni₃Ti and Mo-enriched
7 precipitates are shown in Fig. 7 as a function of aging time; the relative positions and extents
8 of Ni (green), Ti (cyan), and Mo (red) atoms are indicated. In the 0.5-h aged condition, a high
9 number density of Ni₃Ti precipitates was observed, with no detectable Mo-enriched
10 precipitates. As the aging time increases to 24 h, Mo segregation and precipitation at the
11 interface between the Ni₃Ti precipitates and matrix were observed. Increasing the aging time
12 to 60 h results in the coarsening of the Ni₃Ti and Mo-enriched precipitates, forming
13 network-like co-precipitation structures.

14 The bright-field TEM images and corresponding SAED patterns of the Ti/Mo-steel after
15 aging for 0.5, 24, and 60 h at 500 °C are illustrated in Fig. 8a–c, respectively. For comparison,
16 the bright-field images of the Mo-steel in these aged conditions are displayed in Fig. 8d–f. In
17 the 0.5-h aged condition, a high density of dislocations is present in the martensitic matrix of
18 both the Ti/Mo- and Mo-steels (Fig. 8a and d, respectively), and no precipitates are visible in
19 these samples. After aging for 24 h, nanoscale precipitates of two types were observed in the
20 Mo-steel (Fig. 8e): one type with an average diameter of approximately 20 nm (yellow
21 arrows) and the other with an average diameter of less than 10 nm (red arrows). Energy

1 dispersive X-ray spectrometry (EDS) mapping (supplementary Fig. S2) reveals that both
2 types of precipitates are enriched in Mo. The SAED pattern shows two sets of diffraction
3 reflections, which correspond to the A_7B_2 -type ω and A_2B -type Laves phases ($A = \text{Fe, Ni, Co,}$
4 and Cr; B = Mo) [30,31]. Figure 8g displays a HAADF-STEM image of a representative ω
5 precipitate in the Mo-steel in the 24-h aged condition. The atomic arrangement of the
6 precipitate matches elegantly with the simulated structure of ω phase (Fig. 8h), thus
7 providing further supportive evidence for the formation of ω phase in the steels. As the aging
8 time increases to 60 h, the average diameter of the Mo-enriched precipitates in the Mo-steel
9 increases to approximately 25 nm; most of them are located at dislocations (Fig. 8f).
10 Moreover, the diffraction spots corresponding to the ω phase disappear in the SAED pattern,
11 and only those corresponding to the Laves phase were observed (inset in Fig. 8f). By contrast,
12 in the Ti/Mo-steel, the ω phase was observed only in the 60-h aged condition (Fig. 8c), and
13 no Laves phase is detected in all the conditions studied. These observations indicate that Ti is
14 likely to play a crucial role in delaying the precipitation of the ω phase and suppressing the
15 formation of the Laves phase, resulting in a significant size refinement of Mo-enriched
16 precipitates in the Ti/Mo-steel.

17 3.3.3 *Cr-rich precipitates*

18 The temporal evolution of Cr-rich precipitates in the Mo-, Ti-, and Ti/Mo-steels was
19 characterized by APT, and the results are shown in Fig. 9. Cr exhibits a uniform distribution
20 without any segregation in the Ti- and Ti/Mo-steels in the 0.5-h aged condition (Fig. 9e and i,
21 respectively); a clear enrichment was observed in all the other aged conditions, in which the

1 25 at.% Cr isoconcentration surfaces were used to visualize the Cr-rich precipitates. The
2 proximity histograms (Fig. 9d, h, and l) show that the Cr-rich precipitates have a composition
3 of 75Cr–25Fe (at.%), which is in accordance with that of the α' phase [31]. The average radii
4 and volume fractions of Cr-rich precipitates in the three steels are summarized in Fig. 10. The
5 average radius of Cr-rich precipitates in the Mo-steel increases from 0.7 ± 0.1 nm at 0.5 h to
6 2.2 ± 0.2 nm at 24 h and to 2.4 ± 0.2 nm at 60 h, whereas that in the Ti-steel increases from
7 1.6 ± 0.1 nm at 24 h to 1.9 nm at 60 h and that in the Ti/Mo-steel increases from 1.5 ± 0.1 nm
8 at 24 h to 1.8 ± 0.2 nm at 60 h. The volume fraction of Cr-rich precipitates in the Mo-steel
9 increases from 0.1% at 0.5 h to 4.7% at 24 h and to 4.8% at 60 h, whereas that in the Ti- and
10 Ti/Mo-steels at 60 h are 3.1% and 3.8%, respectively. These observations indicate that the Ti-
11 and Ti/Mo-steels have a lower degree of Cr-rich precipitation than the Mo-steel.

12 **4 Discussion**

13 *4.1 Mechanisms for the acceleration of Ni_3Ti precipitation by Mo partitioning*

14 The Ti/Mo-steel has a higher number density and volume fraction of Ni_3Ti precipitates
15 than the Ti-steel in the early stage of precipitation, which is associated with the nanoscale
16 partitioning of Mo atoms to the Ni_3Ti precipitates. These observations suggest that Mo is
17 likely to accelerate the Ni_3Ti precipitation through nanoscale partitioning. According to the
18 classical nucleation theory, the nucleation rate is controlled by the chemical driving force,
19 elastic strain energy, and interfacial energy between the precipitates and matrix [33]. The

1 effect of Mo on the nucleation of Ni₃Ti precipitates is analyzed in terms of the chemical
2 driving force and elastic strain energy.

3 First, the effect of Mo on the chemical driving force for the nucleation of Ni₃Ti is
4 discussed. Fundamentally, the supersaturation of Ni and Ti in the Fe-based solid solution
5 provides the chemical driving force for the Ni₃Ti precipitation. Considering the high
6 concentration of Ni (7.3–7.5 wt.%) in these steels, the chemical driving force for the Ni₃Ti
7 precipitation depends mainly on the degree of supersaturation of Ti in the Fe-based solid
8 solution, which is, in turn, related to the solubility limit of Ti in the solid solution. To
9 quantitatively understand the effect of Mo on the solubility of Ti in the Fe-based solid
10 solution, the isothermal section of the Fe–Ti–Mo ternary phase diagram at 500 °C was
11 calculated using Thermo-calc, as shown in Fig. 11. In the Fe–Ti system, the maximum
12 solubility of Ti in the BCC-Fe is approximately 0.27 at.%. Adding a small amount of Mo to
13 the system reduces the solubility of Ti in BCC-Fe considerably, which decreases to zero at
14 0.6 at.% Mo. In other words, Mo increases the degree of supersaturation of Ti in the Fe-based
15 solid solution, resulting in a high chemical driving force for the Ni₃Ti precipitation. The
16 effect of Mo on the solubility of Ti in the Fe-based solid solution can be analyzed using the
17 Hume–Rothery solid solution model [34]. According to the model, the smaller the difference
18 in the electronegativity and atomic size between the solute and solvent elements, the higher
19 the solubility of the solute [34]. The electronegativity values of Ti, Fe, and Mo are 1.54, 1.83,
20 and 2.16, respectively [35]. When Mo is added to Fe, the average electronegativity value of
21 the Fe–Mo solid solution is higher than that of pure Fe. That is, the difference in the

1 electronegativity between Ti and Fe–Mo solution is larger than that between Ti and Fe, which
2 results in a lower solubility of Ti in the Fe–Mo solid solution than in pure Fe. From the
3 atomic size point of view, when Mo (atomic radius 1.39 Å) is added to Fe (1.26 Å), the
4 difference in the atomic size between Ti (1.47 Å) and Fe-Mo solution is smaller than that
5 between Ti and pure Fe. Thus, Mo would increase the solubility of Ti in BCC-Fe, which can
6 not explain the phase diagram. The above analyses imply that the electronegativity factor is
7 likely to play a more prominent role than the atomic size factor in this case.

8 Second, the effect of Mo on the strain energy of the Ni₃Ti precipitates is analyzed. Our APT
9 results suggest that a strong partitioning of Mo to the Ni₃Ti precipitates occurs in the early
10 stage of precipitation. The atomic radii of Ti and Mo are 1.47 and 1.39 Å, respectively; the
11 Mo partitioning is are likely to change the lattice constants of the Ni₃Ti precipitates. Hence,
12 first-principles calculations were performed to calculate the lattice constants of BCC-Fe,
13 η-Ni₃Ti, and η-Ni₃(Ti,Mo); the calculation results are shown in Fig. 12. The lattice constant
14 of BCC-Fe was calculated to be 2.832 Å, which is consistent with the experimental value
15 (2.87 Å) [36]. For η-Ni₃Ti, the lattice constants were calculated to be $a = 5.004$ Å and $c =$
16 8.159 Å. With the partial substitution of Ti by Mo, the lattice constants decrease to $a = 4.985$
17 Å and $c = 8.179$ Å for Ni₃Ti_{0.75}Mo_{0.25} and $a = 4.971$ Å and $c = 8.205$ Å for Ni₃Ti_{0.5}Mo_{0.5}.
18 Therefore, the partial substitution of Ti by Mo leads to a decrease in the lattice parameter of a .
19 As mentioned earlier, the orientation relationship between the η-Ni₃Ti precipitates and
20 α-martensitic matrix is that of Burgers, i.e., $\{110\}_\alpha // \{0001\}_\eta$ and $\langle 111 \rangle_\alpha // \langle 1\bar{1}20 \rangle_\eta$. The
21 matching planes of $\{110\}_\alpha$ and $\{0001\}_\eta$ were used as a reference, and the lattice mismatch

1 along the parallel $\langle 111 \rangle_\alpha$ and $\langle 1\bar{1}20 \rangle_\eta$ directions was estimated according to the equation $\delta =$
2 $2(d_\eta - d_\alpha)/(d_\eta + d_\alpha)$, where d_η and d_α are the lattice constant of η -Ni₃Ti along the a axis and
3 1.73-fold of the lattice constant of α -martensite, respectively. The lattice mismatch between
4 α -Fe and η -Ni₃Ti_{1-x}Mo_x was estimated to be 2%, 1.6%, and 1.3% for $x = 0, 0.25,$ and $0.5,$
5 respectively. Therefore, the partial substitution of Ti by Mo substantially decreases the lattice
6 mismatch between the precipitates and matrix, decreasing the strain energy for the nucleation
7 of Ni₃(Ti,Mo).

8 According to the classical nucleation theory, the increased chemical driving force and
9 the decreased strain energy decrease the critical energy for the nucleation of Ni₃Ti, leading to
10 an increased nucleation rate in the Ti/Mo-steel. Consequently, the number density of Ni₃Ti
11 precipitates in the Ti/Mo-steel is considerably higher than that in the Ti-steel without the
12 addition of Mo (cf. Fig. 4).

13 *4.2 Mechanism for the size refinement of Mo-enriched precipitates*

14 The TEM and APT results indicate that the Mo-enriched precipitates in the Mo- and
15 Ti/Mo-steels have significantly different microstructures, particularly in terms of precipitate
16 size, number density, and crystal structure. With the addition of 1 wt.% Ti, the average radius
17 of the Mo-enriched precipitates decreases considerably from 13 nm in the Mo-steel to 2 nm
18 in the Ti/Mo-steel, which is accompanied by a significant increase in the precipitate number
19 density. The APT results indicate that in the early stage of precipitation, a high number
20 density of Ni₃Ti precipitates was observed first in the supersaturated solid solution, and the
21 precipitate cores are enriched in Ni and Ti together with a considerable amount of Mo. As the

1 aging time increases, the Mo atoms are rejected from the Ni₃Ti precipitate core to the
2 interface between the Ni₃Ti precipitates and matrix. The rejection of Mo atoms outward the
3 Ni₃Ti precipitates promotes the formation of Mo-enriched precipitates in two manners. First,
4 the Mo enrichment provides the chemical condition for the nucleation of Mo-enriched
5 precipitates. Second, the high number of interfaces between the Ni₃Ti precipitates and matrix
6 provides numerous heterogenous nucleation sites for Mo-enriched precipitates. As a result, a
7 high number density of fine-scale Mo-enriched precipitates was observed in the Ti/Mo-steel
8 (cf. Fig. 7). By contrast, in the Mo-steel, Mo-enriched precipitates are formed mainly at
9 dislocations and grain boundaries; they therefore have a lower number density and larger size
10 than the Mo-enriched precipitates in the Ti/Mo-steel. Therefore, the size refinement of
11 Mo-enriched precipitates is due to the co-precipitation of Ni₃Ti and Mo-enriched precipitates;
12 the first formation of Ni₃Ti precipitates promotes the heterogeneous nucleation of
13 Mo-enriched precipitates, leading to the formation of high number densities of fine-sized
14 Mo-enriched precipitates.

15 *4.3 Mechanisms for the inhibition of Cr-rich precipitates in the Ti- and Ti/Mo-steels*

16 APT indicates that the Cr-rich precipitates have a composition of Cr₇₅Fe₂₅, which is in
17 accordance with the composition of the α' -(Cr,Fe) phase. It is known that the α' phase has a
18 BCC structure and is fully coherent with the martensitic matrix, exhibiting no extra
19 diffraction spots on the SAED patterns [37]. Our TEM results do not indicate any diffraction
20 patterns of Cr-rich precipitates in all the aged conditions studied, which is in good agreement
21 with the characteristics of the α' phase. APT findings also indicate that the microstructures of

1 Cr-rich precipitates in the three steels are significantly different, particularly in terms of
2 precipitate size and volume fraction. In the 60-h aged condition, the average radii of Cr-rich
3 precipitates in the Mo-, Ti-, and Ti/Mo-steels are 2.4, 1.9, and 1.8 nm, respectively, and their
4 volume fractions are 4.8%, 3.8%, and 3.1%, respectively. This observation suggests that the
5 formation of Cr-rich precipitates is significantly inhibited in the Ti- and Ti/Mo-steels, as
6 compared with that in the Mo-steel. It was documented that Cr-rich α' nanoparticles are
7 formed via spinodal decomposition, which is highly dependent on the alloy composition. In
8 this study, the Ni_3Ti precipitates form earlier than the α' nanoparticles in the Ti- and
9 Ti/Mo-steels. Thus, the composition of the matrix after the Ni_3Ti precipitation plays a crucial
10 role in determining the formation of α' nanoparticles; this composition can be estimated from
11 the left side of the proximate histograms of the Ni_3Ti precipitates (cf. Fig. 5). As summarized
12 in Table S1, the most significant difference in the matrix composition among the three steels
13 is the Ni concentration (7.57, 4.88, and 3.94 at.% in the Mo-, Ti-, and Ti/Mo-steels,
14 respectively); this concentration is highly dependent on the formation of Ni_3Ti precipitates,
15 which consumes Ni. Miller et al. reported that the addition of Ni to Fe–Cr-based alloys raises
16 the critical temperature of the miscibility gap [38], which promotes the spinodal
17 decomposition of the Fe–Cr-based alloys. In addition, Ponomareva et al. found that the
18 mechanism for the Ni-enhanced spinodal decomposition is that Ni decreases the stability of
19 Fe–Cr alloys and increases the mixing enthalpy of the alloys [39]. Thus, the high Ni
20 concentration (7.57 at.%) in the matrix of the Mo-steel is likely to facilitate spinodal
21 decomposition by decreasing the stability of the Fe–Cr-based matrix. By contrast, the Ni

1 concentration in the matrix of the Ti- and Ti/Mo-steels is low (4.88 and 3.94 at.%,
2 respectively); spinodal decomposition is significantly inhibited in these alloys. As a result, the
3 volume fraction of Cr-rich precipitates in the Ti- and Ti/Mo-steels is lower than that in the
4 Mo-steel.

5 On the basis of the aforementioned discussion in **Sections 4.1, 4.2, and 4.3**, the
6 co-precipitation pathways of the Mo-, Ti-, and Ti/Mo-steels are summarized in the following
7 text and schematically illustrated in Fig. 13. In the Mo-steel, Cr-rich α' precipitates are
8 formed first, and Mo-enriched ω precipitates are formed at a later stage of precipitation; they
9 eventually transform into Laves-type precipitates. In the Ti-steel, the precipitation of Ni_3Ti
10 occurs first, after which the precipitation of Cr-rich α' precipitates takes place. In the
11 Ti/Mo-steel, a high number density of Ni_3Ti precipitates, which are enriched in Ni, Ti, and
12 Mo, are formed first. As the Ni_3Ti precipitates grow, Mo atoms are rejected from the Ni_3Ti
13 precipitate core to the interface between the Ni_3Ti precipitates and matrix, leading to the
14 heterogenous precipitation of Mo-enriched precipitates on the outer surface of the Ni_3Ti
15 precipitates. Meanwhile, Cr-rich precipitates are formed in the rest of the matrix, resulting in
16 a co-precipitation microstructure consisting of Ni_3Ti , Mo-enriched, and Cr-rich precipitates.
17 Therefore, the formations of these precipitates in the maraging stainless steels are not
18 separated, but rather highly interacted.

19 *4.4 Strengthening mechanisms of Ni_3Ti , Mo-enriched, and Cr-rich co-precipitates*

20 The mechanical results reveal that the Ti/Mo-steel is considerably stronger than the Ti-
21 and Mo-steels. There are three types of precipitates in the Ti/Mo-steel- η - $\text{Ni}_3(\text{Ti},\text{Mo})$,

1 ω -Fe₇Mo₂, and Cr-rich α' precipitates—all of which hinder the glide of dislocations. To gain a
2 fundamental insight into the relationship between the precipitate microstructure and
3 mechanical properties of the Ti/Mo-steel, we model the strengthening mechanisms of these
4 nanoscale co-precipitates.

5 In precipitation strengthening, two types of dislocation-precipitate interactions occur
6 depending on the precipitate size: (i) when the precipitate size is less than the critical size,
7 dislocations cut through (or shear) the precipitates, and (ii) when the precipitate size exceeds
8 the critical value, the Orowan bypassing mechanism dominates the precipitation
9 strengthening. For the shearing mechanism, three factors contribute to the increase in yield
10 strength: coherency strengthening ($\Delta\sigma_{\text{coherency}}$), modulus strengthening ($\Delta\sigma_{\text{modulus}}$), and order
11 strengthening ($\Delta\sigma_{\text{order}}$). Coherency and modulus strengthening occur before the dislocation
12 shears the precipitates, the order strengthening occurs during shearing. Therefore, the larger
13 value of ($\Delta\sigma_{\text{coherency}} + \Delta\sigma_{\text{modulus}}$) or $\Delta\sigma_{\text{order}}$ is expected to contribute to the strength increment
14 from the shearing mechanism [40]. Because the shearing and bypassing mechanisms occur
15 separately, the strengthening is determined by whichever value between the $\Delta\sigma_{\text{shearing}}$ or
16 $\Delta\sigma_{\text{Orowan}}$ is lower. The maximum increase in the yield strength is attained when the values of
17 $\Delta\sigma_{\text{shearing}}$ and $\Delta\sigma_{\text{Orowan}}$ are equal at the critical precipitate size, given a fixed volume fraction.
18 The critical radii for the Ni₃Ti, ω , and α' precipitates are estimated to be 4.4, 7.5, and 6.0 nm,
19 respectively (see Supplementary material for calculation details). According to the APT
20 results (Table S2), the average radii of the Ni₃Ti, ω and α' precipitates in the Ti/Mo-steel are
21 2.1, 1.8, and 1.8 nm, respectively; all these values are smaller than the critical values. Hence,

1 the particle shearing mechanism should be operative in the Ti/Mo-steel. The strengthening
2 contributions from the three types of precipitates were calculated (see Supplementary
3 material for calculation details), and the results are shown in Fig. 14. The sum of $\Delta\sigma_{\text{coherency}}$
4 and $\Delta\sigma_{\text{modulus}}$ makes a small contribution to the increase in the yield strengths, which are 400,
5 116, and 60 MPa for the Ni_3Ti , ω , and α' precipitates, respectively. By contrast, order
6 strengthening is a major contributor to precipitation strengthening, contributing
7 approximately 896, 376, and 362 MPa for the Ni_3Ti , ω , and α' precipitates, respectively. On
8 the basis of the reasonable assumption that the contributions from the three types of
9 precipitates are additive, the total precipitation strengthening, $\Delta\sigma_{\text{total}}$, is estimated using the
10 superposition expression [41]:

$$11 \quad \Delta\sigma_{\text{total}} = \sqrt{(\Delta\sigma_{\text{Ni}_3\text{Ti}})^2 + (\Delta\sigma_{\omega})^2 + (\Delta\sigma_{\alpha'})^2} \quad (3)$$

12 where $\Delta\sigma_{\text{Ni}_3\text{Ti}}$, $\Delta\sigma_{\omega}$, and $\Delta\sigma_{\alpha'}$ are the strengthening contributions of the Ni_3Ti , Mo-enriched ω ,
13 and Cr-rich α' precipitates, respectively. The calculated value of $\Delta\sigma_{\text{total}}$ from the three types of
14 precipitates is 1047 MPa, very close to the experimental value (993 MPa, the difference
15 between the yield strengths in the peak-aged and as-quenched conditions), indicating that the
16 precipitate shearing mechanism is operative in the Ti/Mo-steel in the peak-aged condition.

17 **5. Conclusions**

18 In this study, we investigated the precipitate microstructure and mechanical properties of
19 maraging stainless steels strengthened by nanoscale Ni_3Ti (η phase), Mo-enriched (ω phase),
20 and Cr-rich (α' phase) co-precipitates. The following conclusions are drawn from the study:

- 1 1. APT results indicate that Mo partitions to the Ni₃Ti precipitate core in the early stage of
2 precipitation, which substantially accelerates the Ni₃Ti precipitation. The thermodynamic
3 and first-principles calculations indicate that Mo not only enhances the chemical driving
4 force, but also reduces the strain energy for the nucleation of Ni₃Ti, leading to a higher
5 number density of Ni₃Ti precipitates in the Ti/Mo-steel than in the Ti-steel.
- 6 2. As the precipitation reaction proceeds, the first formation of the Ni₃Ti precipitates leads
7 to the rejection of Mo atoms outward from the Ni₃Ti precipitate core to the Ni₃Ti/matrix
8 interface, which results in the heterogeneous precipitation of Mo-enriched precipitates on
9 the outer surface of the Ni₃Ti precipitates. This results in a significant size refinement of
10 the Mo-enriched precipitates in the Ti/Mo-steel as compared with those in the Mo-steel.
- 11 3. The formation of Ni₃Ti precipitates also influences the precipitation of Cr-rich α'
12 precipitates owing to the change in the phase stability of the matrix. The APT results
13 indicate that the Ni₃Ti precipitation consumes a large amount of Ni, leading to a lower Ni
14 concentration in the matrix of the Ti- and Ti/Mo-steels, compared with that in the
15 Mo-steel. The low Ni concentration enhances the stability of the matrix and inhibits the
16 spinodal decomposition of the Ti- and Ti/Mo-steels. As a result, the volume fraction of
17 Cr-rich precipitates in the Ti- and Ti/Mo-steels is much lower than that in the Mo-steel.
- 18 4. With the cooperative strengthening of Ni₃Ti, Mo-enriched, and Cr-rich co-precipitates,
19 the Ti/Mo-steel exhibits a yield strength of 1732 MPa at room temperature and over 1100
20 MPa at 500 °C, demonstrating a high strength over a wide temperature range. The
21 strengthening mechanisms of Ni₃Ti, Mo-enriched, and Cr-rich precipitates are

1 quantitatively evaluated in terms of the precipitate shearing and Orowan dislocation
2 looping mechanisms. Modeling of the strengthening mechanisms shows that the
3 precipitate shearing mechanism is operative in the Ti/Mo-steel in the peak-aged condition
4 and that the strengthening of Ni₃Ti precipitates is a major contributor to the total
5 precipitation strengthening.

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- 22

1 **Figure captions**

2 **Fig. 1** Mechanical properties of the Mo-, Ti-, and Ti/Mo-steels. (a) Hardnesses as a function
3 of aging time at 500 °C, (b) tensile stress-strain curves at room temperature, (c) tensile
4 stress-strain curves at 500 °C, and (d) UTS and YS of the three steels as a function of testing
5 temperature.

6 **Fig. 2** Bright-field TEM images of the steels in the different aged conditions: (a) Ti-steel, 0.5
7 h, (b) Ti/Mo-steel, 0.5 h, (c) Ti-steel, 24 h, (d) Ti/Mo-steel, 24 h, (e) Ti-steel, 60 h, and (f)
8 Ti/Mo-steel, 60 h.

9 **Fig. 3** HAADF-STEM images of η -Ni₃Ti precipitates in the (a) Ti-steel and (b) Ti/Mo-steel
10 after aging for 60 h, and (c) and (d) are the corresponding FFT patterns of (a) and (b),
11 respectively.

12 **Fig. 4** APT characterization of Ni₃Ti-type precipitates in the Ti- and Ti/Mo-steels: (a) Ti-steel,
13 0.5 h, (b) Ti-steel, 24 h, (c) Ti-steel, 60 h, (d) Ti/Mo-steel, 0.5 h, (e) Ti/Mo-steel, 24 h, and (f)
14 Ti/Mo-steel, 60 h. (g) and (h) are number densities and volume fractions of Ni₃Ti precipitates
15 as a function of aging time.

16 **Fig. 5** Proximity histograms of the Ni₃Ti precipitates in the different aged conditions: (a)
17 Ti-steel, 0.5 h, (b) Ti-steel, 24 h, (c) Ti-steel, 60 h, (d) Ti/Mo-steel, 0.5 h, (e) Ti/Mo-steel, 24
18 h, and (f) Ti/Mo-steel, 60 h.

19 **Fig. 6** Mo atom distributions in the Ti/Mo-steel after aging for (a) 0.5 h, (b) 24 h, and (c) 60 h,
20 and precipitate microstructures of Ni₃Ti and Mo-enriched co-precipitates in the (d) 24-h and
21 (e) 60-h aged conditions.

22 **Fig. 7** 1-nm-thick atom maps and isoconcentration surfaces through the centers of Ni₃Ti and
23 Mo-enriched precipitates of the Ti/Mo-steel after aging for (a) 0.5 h, (b) 24 h, and (c) 60 h.

24 **Fig. 8** TEM and STEM characterization of the Ti/Mo- and Mo-steels in the different aged
25 conditions: (a) Ti/Mo-steel, 0.5 h, (b) Ti/Mo-steel, 24 h, (c) Ti/Mo-steel, 60 h, (d) Mo-steel,

1 0.5 h, (e) Mo-steel, 24 h, and (f) Mo-steel, 60 h. (g) is a HAADF-STEM image of a ω
2 precipitate in (e), and (h) is the simulated structure of ω phase.

3 **Fig. 9** APT characterization of Cr atoms and Cr-enriched precipitates in the different aged
4 conditions: (a) Mo-steel, 0.5 h, (b) Mo-steel, 24 h, (c) Mo-steel, 60 h, (e) Ti-steel, 0.5 h, (f)
5 Ti-steel, 24 h, (g) Ti-steel, 60 h, (i) Ti/Mo-steel, 0.5 h, (j) Ti/Mo-steel, 24 h, and (k)
6 Ti/Mo-steel, 60 h. (d), (h), and (l) are the proximity histograms of the Mo-, Ti-, and
7 Ti/Mo-steels, respectively, in the 60-h aged condition.

8 **Fig. 10** (a) Average radii and (b) volume fractions of Cr-rich precipitates in Mo-, Ti-, and
9 Ti/Mo-steels as a function of aging time.

10 **Fig. 11** The isothermal section of Fe-Ti-Mo ternary phase diagram at 500 °C.

11 **Fig. 12** Lattice constants of Ni_3Ti , $\text{Ni}_3\text{Ti}_{0.75}\text{Mo}_{0.25}$, $\text{Ni}_3\text{Ti}_{0.5}\text{Mo}_{0.5}$, and BCC-Fe determined by
12 first-principles calculations.

13 **Fig. 13** Schematics showing the co-precipitation processes of the Mo-, Ti-, and Ti/Mo-steels.

14 **Fig. 14** Theoretical contributions of the coherency strengthening, modulus strengthening, and
15 order strengthening of the Ni_3Ti , ω , and α' precipitates in the Ti/Mo-steel. The experimental
16 value of precipitation strengthening is included for comparison.

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