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Published in:
Materials Today

Published: 01/04/2017

Document Version:
Final Published version, also known as Publisher’s PDF, Publisher’s Final version or Version of Record

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Publication record in CityU Scholars:
Go to record

Published version (DOI):
10.1016/j.mattod.2016.07.002

Publication details:

Citing this paper
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Co-precipitation of nanoscale particles in steels with ultra-high strength for a new era

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Advanced ultra-high strength steels are highly desirable for a wide range of engineering applications. Nanoscale co-precipitation strengthening in steels has received increasing attention in recent years and has become a new cornerstone for the development of advanced steels with superior combination of mechanical, welding, and irradiation properties for a new era. In this review, we highlight recent advances in computation-aided alloy design, nanostructural characterization, and unique properties of newly developed nanoscale co-precipitation-strengthened steels. In particular, our emphasis is on elucidating alloy design strategies, the co-precipitation mechanism, and cooperative evolution of multiple types of nanoparticles, and the correlation between nanostructures and bulk steel properties. Finally, future research areas for this class of nanostructured steels are critically discussed.

Introduction
Advanced structural steels are essential to the modern world, and their continuous innovation is critical to moving toward a sustainable future. Steelmaking, however, is known as one of the world’s largest industrial sources of CO₂ emission and environmental pollution. With the now unprecedented environmental challenges facing mankind, such as global warming and smog, it is critical to develop and use ultra-high strength (>1000 MPa tensile strength) steels to dramatically reduce the amount of common low-strength steels in use at the present time. To date, considerable efforts have been devoted to improve the strength of steels, and there have been significant advances in the Fe–C- and Fe–Ni-based martensitic steels. For example, medium-carbon martensitic steels such as 4340 and 300 M have good strength, but suffer from poor weldability due to the high carbon content (0.3–0.6 wt.%)[1]. Secondary hardening and maraging steels have good welding properties, but both are too expensive for general use because of the high concentrations of expensive alloying additions, including Co and Ni[1]. Therefore, traditional ultra-high strength steels are either prohibitively expensive or suffer from poor weldability, and it is important to develop weldable and inexpensive alternatives.

Basically, strengthening crystalline materials involves the controlled creation of internal defects and boundaries to impede the motion of dislocations[2–6]. Among the various strengthening methods, nanoparticle strengthening has been proved to be one of the most effective approaches to enhance the strength of steels while minimizing the consumption of carbon and alloy additions[7], the degree of which can be controlled by compositional optimization[8–13] and/or thermomechanical processing[12–18]. Moreover, nanoparticles dissolved in the matrix during welding can be easily reprecipitated as nanoparticles upon cooling and/or post-weld processing, thus providing a promising way to recover mechanical properties of the weld[19]. Recent development of nanoscale analytical tools such as the atom probe tomography (APT) [20–22] and aberration (Cs)-corrected transmission electron microscopy (Cs-TEM) [23,24] enables alloy characterization at the atomic scale and provides new opportunities for precisely engineering the nanostructures. It has now been realized that the body-centered cubic (bcc) ferritic/martensitic steels are ideal...
materials for strengthening by coherent nanoparticles, which can precipitate on a sufficiently fine scale (less than 5 nm in diameter) to provide an extremely high strengthening response [25–27]. In particular, the co-precipitation of multiple types of nanoparticles is more attractive than precipitation of a dispersion of a single type of nanoparticles, since the co-precipitation approach may lead to a superior combination of different properties resulting from the synergistic combination of the multiple types of nanoparticles with different compositions, microstructures, and micromechanical properties [28–45]. As a result, the development of nanoscale co-precipitation-strengthened steels has received growing interest from both academia and industry.

In the current review, we aim at highlighting recent important developments in the computation-aided alloy design, precipitation of nanostructures, and unique properties of the nanoscale co-precipitation-strengthened ferritic/martensitic steels. Oxide-dispersion-strengthened (ODS) steels fabricated by mechanical alloying and nanograined steels fabricated by severe plastic deformation will not be included because of the atypical and expensive processing route [46]. In particular, our focus includes nanostructural design with the aid of computational techniques combined with atomic-scale characterization using state-of-the-art experimental tools such as APT and Cs-TEM, and the mechanistic understanding of the nanoscale co-precipitation mechanism in steels with different alloy compositions as well as the correlation between nanostructure and bulk properties, including tensile, creep, welding, and irradiation properties. Finally, prospects for the future of this class of nanostructured steels will be highlighted.

**Computation-aided alloy design of co-precipitation-strengthened steels**

Traditionally, new steels are developed through a ‘trial and error’ approach, which requires a systematical production of alloys with varied compositions and heat treatments. This approach is usually costly and time-consuming, especially for multicomponent steels. With the improved understanding of the composition-processing-structure-property relationship and the advent of more powerful and reliable modern computational techniques, alloy design is now increasingly oriented to the integrated computational-prediction and experimental-validation approach [47–49], as schematically illustrated in Fig. 1. In particular, computational techniques such as thermodynamic and first-principles calculations provide useful guidelines for the alloy design, while the state-of-the-art analytical tools such as APT and Cs-TEM enable detailed characterization of these steels on the nanometer scale.

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**The integrated computational-prediction and experimental-validation approach**

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**FIGURE 1**

The integrated computational-prediction and experimental-validation approach for the development of nanoscale co-precipitation-strengthened steels.
The design of nanoscale co-precipitation-strengthened steels requires precise control of the size, number density, and spatial distribution of various types of nanoparticles [50]. Coherent nanoparticles are preferred because they have a tendency to nucleate uniformly in the matrix, achieving very high number densities and ultra-fine particle sizes [28–45]. Typically, there are two groups of particle structures that are capable of high coherency with the bcc-Fe matrix: one is the bcc or bcc-derived groups (e.g., bcc-Cu, B2-NiAl, and L21-Ni2AlTi and Ni2AlMn) and the other is the hcp group (e.g., Ni3Ti and Mo2C). The coherency of the first group is permitted by a near coincidence in the cube planes of both the particles and bcc-Fe matrix, while that of the second group is allowed by a near-coincidence of the particle close-packed direction and the bcc-Fe cube direction [51]. In contrast, less coherent particles such as FeCr, Fe3Mo, Fe3C, and Fe2W, usually precipitate in a coarse form with weak strengthening efficiency and even cause embrittlement due to interfacial precipitation, and therefore should be minimized in alloy design [52]. The success of this computation-aided alloy design approach has been demonstrated in several studies. For example, Saha and Olson applied ThermoCalc to develop a new class of ultra-tough, weldable, secondary hardened steels strengthened by Cu nanoparticles (2–5 nm radius) and (Mo,Cr,V)2C carbides [28]. Xu et al. developed a general computational alloy design program based on the thermodynamic and physical metallurgical principles and coupled with a genetic optimization scheme, which has been developed to apply new ultrahigh-strength maraging stainless steels strengthened by multiple nanoparticles, including the MC carbides, Cu particles, and Ni3Ti intermetallics [41]. Jiao et al. used Thermo-Calc to develop a 1.9 GPa strength steel strengthened by co-precipitation of B2-NiAl and bcc-Cu nanoparticles with sizes of 1–5 nm [34]. Liaw et al. developed a new class of ferritic superalloys strengthened by hierarchical NiAl and Ni2TiAl co-precipitates by combining thermodynamic and first-principles calculations [53]. Millán et al. demonstrated that the combination of ab initio calculations and high-resolution microstructure characterization enables the design of advanced lean maraging steels strengthened by NiMn and Ni2AlMn nanoparticles [44]. The compositions of some representative steels strengthened by nanoscale co-precipitation are summarized in Table 1, with the principle strengthening phases listed.

### Atomic-level characterization of the nanostructures in steels

In the following section, the atomic level characterization of the co-precipitated nanostructure using state-of-the-art analytical tools such as APT and Cs-TEM will be presented. Because a vast amount of work has been carried out in this direction, our discussion is limited only to recent examples.

#### Co-precipitation of bcc-Cu and B2-NiAl nanoparticles

It has been documented that initially precipitated Cu nanoparticles have a metastable bcc structure and are coherent with the bcc-Fe matrix, which gradually transform into a 9R and finally fcc structure at the later stages of growth [54–62]. NiAl nanoparticles possess an ordered cubic B2 crystal structure, which also satisfies the lattice coherency requirement in the bcc-Fe matrix [63–67]. Through the optimization of alloy composition, co-precipitation of bcc-Cu and B2-NiAl nanoparticles can be achieved in multi-component steels. In Fe–Cu-based steels with a minor amount of Ni and Al, Cu nanoparticles precipitate first from the supersaturated bcc-Fe matrix, and both Ni and Al tend to segregate at the interface between the Cu nanoparticles and the matrix [28–31,58–61]. Long-term aging leads to the precipitation of NiAl nanoparticles in addition to the Cu nanoparticles, forming Cu/ NiAl co-precipitates with diameters larger than 10 nm (Fig. 2a) [31]. With increasing Ni and Al concentrations, Cu/NiAl co-precipitates can be observed at an earlier stage of precipitation, with smaller (5–10 nm) particle size (Fig. 2b) [32,33,37–40]. With further increase in Ni and Al concentrations, a high number density of Cu/NiAl co-precipitates with ultra-fine sizes of 1–5 nm can be detected, together with a significant amount of isolated NiAl nanoparticles without any Cu nanoparticles associated with them (Fig. 2c) [34].

It is interesting to point out that although Cu/NiAl co-precipitates can be formed in a wide range of composition, precipitation mechanisms of Cu/NiAl co-precipitates can be significantly different, depending on the Cu/Ni and Cu/Al ratios. The two precipitation pathways of the Cu/NiAl co-precipitates are summarized as follows and schematically illustrated in Fig. 2d [68].

- In steels with high Cu/Ni and Cu/Al ratios: The high Cu concentration in such steels provides a high chemical driving force for the formation of Cu-rich nanoparticles. Initially, the

### Table 1

| Composition and principle strengthening phases of representative nanoscale co-precipitation-strengthened steels (wt.%) |
| Cu | Ni | Mn | Al | Ti | Co | Mo | Cr | V | W | Nb | Zr | Si | B | C | Strengthening phase | Ref. |
| 3.65 | 6.5 | – | – | – | – | 0.6 | 1.84 | 0.1 | – | – | – | – | – | 0.05 | Cu + Mo2C | [28] |
| 1.34 | 2.71 | 0.47 | 0.60 | – | – | 0.07 | 0.46 | 0.05 | Cu + NbC | [29] |
| 2.09 | 2.83 | 0.51 | – | – | – | 0.07 | 0.5 | 0.05 | Cu + NiAl | [31] |
| 3 | 4 | 3 | 1.5 | – | – | 0.07 | 0.53 | 0.05 | Cu + NiAl | [32] |
| 1.5 | 5 | 3 | 2 | – | – | 1.5 | 1.5 | 0.07 | 0.01 | 0.05 | NiAl + Cu | [34] |
| 2.22 | 4.14 | 0.61 | 0.03 | 0.53 | 2.09 | 0.51 | 11.98 | 0.01 | – | 0.11 | 0.57 | 0.09 | Cu + Ni2Ti | [41] |
| – | 10 | 6.5 | 2 | – | 3.4 | 10 | – | – | – | 0.25 | 0.01 | – | NiAl + Ni2AlTi | [43] |
| – | 9.05 | 0.7 | 0.35 | – | – | 2.0 | – | – | – | – | 0.05 | – | – | NiAl + Ni2Ti | [45] |
| – | 2.95 | 12.1 | 0.75 | – | – | – | – | – | – | – | – | 0.01 | – | 0.01 | NiMn + Ni2AlMn | [44] |
| – | 2.06 | 11.9 | 0.12 | 1.09 | – | 1.12 | – | – | – | – | – | 0.06 | – | 0.01 | NiMn + Ni2Ti | [27] |
Figure 2

Co-precipitation of Cu and NiAl nanoparticles in Fe–Cu–Ni–Al-based steels: (a) Fe–2.09Cu–2.83Ni–0.68Al-based (wt.%) steel after aging for 1, 4, and 1024 h at 500 °C [31], (b) Fe–3Cu–4Ni–1.5Al-based steel after aging for 2 h at 550 °C [32], and (c) Fe–1.5Cu–5Ni–2Al-based steel after aging for 2 h at 550 °C [34]. (d) The two pathways of the co-precipitation of Cu and NiAl nanoparticles in steels with different Cu/Ni and Cu/Al ratios [68].
Cu-rich nanoparticles, with some amounts of Ni and Al, nucleate first from the supersaturated solid solution. As the particles grow, both Ni and Al segregate at the Cu particle/matrix interface, which has been found to reduce the interfacial energy of the Cu nanoparticles, thereby promoting their nucleation [28–33,37–40,58–61]. As a result, a small amount of Ni addition results in a dramatic refinement of the Cu nanoparticle size, accompanied by a significant increase in particle number density [61]. In addition, the enrichment of Ni and Al at the Cu particle/matrix interface leads to the heterogeneous nucleation of NiAl nanoparticles, resulting in the formation of Cu/NiAl co-precipitates.

- In steels with low Cu/Ni and Cu/Al ratios: NiAl-based nanoparticles, enriched in Ni and Al together with a significant amount of Cu, nucleate first from the supersaturated solid solution. Since Cu has marginal solubility in the α-Fe matrix, it can easily be incorporated in the NiAl precipitation process. As the precipitation reaction proceeds, the first formation of NiAl-based nanoparticles leads to the rejection of Cu solutes toward the nanoparticle surface, resulting in the heterogeneous precipitation of Cu nanoparticles on the outer surface of NiAl nanoparticles, thus forming Cu/NiAl co-precipitates [34].

Co-precipitation of B2-NiAl and L21-Ni2AlTi nanoparticles

Fe–Ni–Al-based ferritic steels strengthened by B2-NiAl nanoparticles are candidates for elevated-temperature structural applications because of their low cost, small thermal expansion, good oxidation resistance, and high thermal conductivity [63–67]. It has been shown recently that through a small addition of Ti to such alloys, dual-phase NiAl/Ni2AlTi co-precipitates can be formed [42,43,69]. Solid-state aging of a Fe–18.2Ni–8.1Al–2.0Ti-based steel at 700°C leads to a hierarchical microstructure, but initially with the primary B2-NiAl nanoparticles and later with L21-Ni2AlTi nanoparticles nucleating and growing within the former [69]. After rapid solidification (Fig. 3a), only primary B2-NiAl nanoparticles with diameters ranging between 10 and 20 nm are embedded in the bcc Fe-matrix. Subsequent aging for 1 h at 700°C leads to the formation of nanometer-sized L21-Ni2AlTi precipitates seen as green regions within the primary B2-NiAl particles (Fig. 3b). The B2-NiAl nanoparticles display a cuboidal shape with edge length between 25 and 50 nm, whereas the size of the L21-Ni2AlTi substructures is estimated to be ~5 nm. Further aging for 3 h at 700°C results in a well-established substructure of L21-Ni2AlTi within the primary B2-NiAl particles (Fig. 3c). The B2-NiAl particles have coarsened with an increase in edge length to values between 40

**FIGURE 3**

Dark-field TEM images for the Fe–8.1Al–12.2Cr–1.9Mo–18.2Ni–2.0Ti (wt.%) alloy in the (a) as-quenched, (b) aging for 1 h at 700°C, and (c) aging for 3 h at 700°C. (d) Core loss energy-filtered TEM images of the alloy after aging for 10 h at 700°C [69].
TEM images and APT reconstructions showing size and spatial distribution of nanoparticles in the martensitic matrix after aging at 450°C for 65 h: (a) NiMn nanoparticles in low-Al steel, (b) NiMn and Ni$_2$AlMn nanoparticles in medium-Al steel, and (c) Ni$_2$AlMn nanoparticles in high-Al steel [44].
and 100 nm, whereas the L2₁-Ni₂AlTi substructures adopt a plate-shaped geometry with a width of 5–10 nm and an aspect ratio of ~1/5. After 10 h of aging at 700°C, the hierarchical microstructure is fully developed, as illustrated by energy-filtered TEM images in Fig. 3d. The edge length of the B₂-NiAl particles increases to 60–200 nm, whereas the L₂₁-Ni₂AlTi substructures remain mostly plate shaped with a size range from 15 to 20 nm. Therefore, the subsequent aging at 700°C yields nucleation and growth of the L₂₁-Ni₂AlTi substructures within the primary B₂-NiAl nanoparticles, leading to a microstructure exhibiting three types of hierarchy: (i) a structural hierarchy due to chemical ordering, with a chemically disordered matrix of bcc-Fe, the nearest-neighbor B₂-ordered NiAl, and the next nearest-neighbor L₂₁-Ni₂AlTi within B₂-NiAl, (ii) a dimensional hierarchy with the continuous bcc-Fe matrix, B₂-NiAl particles with dimensions of 60–200 nm, and L₂₁-Ni₂AlTi substructures with dimensions of 15–20 nm, and (iii) a spatial hierarchy where the B₂-NiAl particles are embedded in the bcc-Fe matrix and the L₂₁-Ni₂AlTi substructures nucleate and grow only within B₂-NiAl particles [69].

**Co-precipitation of B₂-NiMn and L₂₁-Ni₂AlMn nanoparticles**

Fe–Ni–Mn maraging steels have attracted increasing interest because of their economic aspects [70]. It is found that Mn content of 6–12 wt.% allows the reduction of Ni content to less than 5 wt.%, resulting in a new generation of low-cost maraging steels [27]. Moreover, small additions of Al can further change the precipitate type from B₂-NiMn to L₂₁-Ni₂AlMn. The precipitation microstructure of the Fe–3Ni–12Mn–xAl-based (x = 0.1, 0.8, and 1.3 wt.%) steels is presented in Fig. 4 [44]. In the low-Al steel, the coarse
particles have an average composition of 50Ni–35Mn–12.5Fe–
5Ti–2.5Al (at.%), suggesting the formation of the NiMn-type
particles. In the high-Al steel, a high number density of fine
particles with an average composition of 50Ni–20Mn–20Al–
10Fe (at.%) can be observed, implying the precipitation of Heusler
Ni3AlMn nanoparticles. In comparison, medium-Al steels show
co-precipitation of both coarse NiMn and fine Ni2AlMn particles.
Precipitation of NiMn and Ni2AlMn nanoparticles has also been
confirmed by TEM. It is important to point out that the precipitate
transformation from NiMn to Ni2AlMn has a significant impact
on particle dispersion and age-hardening response of the steels. In
the high-Al steel, a uniform distribution of much finer nanoparticles
(average diameter 3–5 nm) forms, in contrast to medium- and low-
Al steels with nanoparticles of average diameters of 5–10 and 10–
20 nm, respectively. Simultaneously, the number density of
Ni2AlMn nanoparticles in the high-Al steel is almost one order
of magnitude higher than that of the NiMn nanoparticles obtained
in the low-Al alloys. The precipitation microstructure of NiMn and
Ni2AlMn nanoparticles can be explained by the elastic misfit be-
tween the nanoparticles and the matrix. First-principles calcula-
tions reveal small and positive misfit parameters of 3% and 2% for
the NiMn/matrix and Ni2AlMn/matrix, respectively. The low misfit
between Ni2AlMn nanoparticles and the matrix enables a smaller
critical nucleation radius according to the classical nucleation
theory. As a result, the high-Al steel exhibits a much finer particle
dispersion of Ni2AlMn than that of NiMn in the low-Al steel,
resulting in a higher age-hardening response [44].

**Co-precipitation of η-Ni3Ti and B2-NiAl nanoparticles**
It is well known that η-Ni3Ti nanoparticles are one of the most
common and effective strengthening phases in maraging steels
[71]. If a certain amount of Al (usually 0.5–2 wt.%) is added to Fe–
Ni–Ti maraging steels, the co-precipitation of η-Ni3Ti and B2-NiAl
nanoparticles can be observed. For example, the precipitation microstructure of a Fe–9Ni–0.35Ti–0.7Al-based steel after aging
for 10 h at 525°C is shown in Fig. 5a [45]. APT reveals two
populations of particles: one with spherical morphology enriched
in Ni and Al and the other with an elongated shape enriched in Ni,
Ti, and Al. Proximity histograms [72] of these two types of particles
are illustrated in Fig. 5b and c, respectively [45]. The atomic ratio of
Ni/(Al + Fe) in the spherical particles is approximately 1:1, suggesting
that these spherical nanoparticles are of the NiAl-type with
certain amounts of Fe substituted for Al. The Ni/(Ti + Al) atomic
ratio in the elongated particles is close to 3:1, consistent with the
formation of the Ni3(Ti,Al) phase with Al occupying the Ti sub-
lattice.

More interestingly, when Cu is added to the η-Ni3Ti- and B2-
NiAl-strengthened steels, the precipitation behavior becomes
more complex [73]. Cu has a significant influence on the precipita-
tion kinetics and microstructure of NiAl- and Ni3Ti-type nanopar-
ticles. However, its effect on the nucleation mechanism of
these two types of precipitates is different. For the NiAl-type
nanoparticles, Cu is incorporated by substituting for Al and thus
reduces the lattice misfit between NiAl(Cu) particles and the
matrix, thereby decreasing the critical nucleation energy of
NiAl-type nanoparticles. In comparison, for Ni3Ti-type nanopar-
ticles, Cu acts as a nucleation site for the heterogeneous precipita-
tion of Ni3Ti by forming independent Cu-rich nanoclusters [73].

**Properties of various co-precipitation-strengthened steels**

**Tensile properties**
Nanoparticle strengthening is a promising approach to impede the
motion of dislocations, and thereby improve the strength of steels
[50]. For co-precipitation-strengthened steels, more than one type
of nanoparticles can contribute to the strengthening effect. Particle
dispersion may also be refined due to the synergistic combina-
tion of different types, sizes, and distributions of nanoparticles. As
a result, the strengthening effect of nanoscale co-precipitates is
usually more pronounced than that of the dispersion of a single
type of nanoparticles. More importantly, ultra-fine nanoparticles
with size less than 5 nm would usually not easily induce crack
initiation; thus, another advantage of having a fine dispersion of
nanoparticles is effective strengthening without significantly
sacrificing the ductility, leading to the development of advanced
steels with a good combination of strength and ductility [74]. For
example, the engineering stress–strain curve of a bcc-Cu/B2-NiAl
co-precipitation-strengthened steel is shown in Fig. 6a, and the

**FIGURE 6**
(a) Tensile stress–strain curve of Cu/NiAl-strengthened steel and
corresponding fracture surfaces [34], and the curve of an as-quenched base
steel without any Cu/NiAl precipitates is included for comparison [36].
(b) Comparison of the yield strength and elongation of representative
nanoscale co-precipitation-strengthened steels with those of common
commercial steels [75].
corresponding fracture surfaces are shown in the insets [34]. The steel exhibits an ultimate tensile strength of ~1.9 GPa, an elongation-to-failure of ~10%, and a reduction in area of ~40%, indicating a good combination of strength and ductility [34]. From the fractured samples, obvious necking and large reductions in area are clearly observed, and the fracture surface shows a micro-void coalescence fracture mode with numerous fine dimples, indicative of ductile fracture. The yield strength and elongation-to-failure data for several representative nanoscale co-precipitation-strengthened steels are summarized in Fig. 6b, which include the nanoparticles bcc-Cu, B2-NiAl, L21-Ni3AlMn, η-Ni3Ti, and M2C carbides. For comparison, the yield strength and elongation-to-failure data of typical steels reported in the literature, such as the transformation-induced-plasticity (TRIP) steels, dual and complex phase (DP-CP) steels, high-strength low-alloy (HSLA) steels, and martensitic steels (MART), are also included [75]. These nanoscale co-precipitation-strengthened steels are distinctly superior to the aforementioned typical steels, in terms of combination of strength and ductility. We expect this class of nanostructured steels to have great potential for structural applications.

Creep resistance
Creep resistance is one of the most important mechanical properties for elevated-temperature structural applications such as components for steam turbines in thermal power plants [76]. Although NiAl-strengthened ferritic steels show promising potential as steam turbine materials in thermal power plants because of their good thermal conductivity, low thermal expansion, and reasonable cost, these alloys suffer from insufficient creep resistance at 973 K for steam turbine applications [63].

Recently, it has been found that hierarchical NiAl/Ni2AlTi co-precipitates can significantly improve creep properties of the aforementioned alloys [42,43,69]. The creep resistance (steady-state creep rate and time to rupture as a function of applied stress) of the NiAl/Ni2AlTi-strengthened steel at 973 K was compared with those of the NiAl-strengthened steel and conventional ferritic steels of P92, P122, T91, T122, and 12Cr in Fig. 7 [43]. The steady-state creep rate of the NiAl/Ni2AlTi-strengthened steel at 973 K is reduced by more than four orders of magnitude at the same stress (Fig. 7a), as compared to those of NiAl-strengthened steel and other conventional ferritic steels. The threshold stress for NiAl/Ni2AlTi-strengthened steel at strain rates above 1 × 10⁻⁸ s⁻¹ is ~186 MPa, which is more than twice that of the NiAl-strengthened steel (69 MPa) [43]. Moreover, the time to rupture for NiAl/Ni2AlTi-strengthened steel at 142 MPa (2675 h) is more than two orders of magnitude higher than that for NiAl-strengthened steel FBB8 at 140 MPa (~4.5 h), indicating that NiAl/Ni2AlTi-strengthened steel is much more creep resistant than NiAl-strengthened steels [43]. The mechanisms for the improved creep resistance in the NiAl/Ni2AlTi-strengthened steel can be explained by the lattice-strain evolution obtained from in situ neutron diffraction. Neutron diffraction results demonstrate that the hierarchical NiAl/Ni2AlTi co-precipitates can effectively transfer the load from the Fe matrix during loading and creep deformation,
whereas there is no clear load transfer from the matrix to the NiAl nanoparticles in NiAl-strengthened steels [43]. As a result, the diffusional flow along the matrix-particle interface is less significant in NiAl/Ni3AlTi-strengthened steel than in NiAl-strengthened steel, resulting in much improved creep resistance for NiAl/Ni3AlTi co-precipitation-strengthened steel. These results provide a new alloy design strategy using the novel concept of hierarchical NiAl/ Ni3AlTi co-precipitates for developing creep-resistant ferritic alloys.

Welding properties

One problem with most traditional high-strength carbon steels is the poor weldability due to the formation of a brittle heat-affected zone (HAZ) adjacent to the weld [77]. In particular, the welding of these steels requires expensive welding controls to prevent welding cracking, which results in a high cost. One can overcome this problem by using steels with low carbon contents and by enhancing the strength with nanoparticles. The weldability of nanoparticle-strengthened steels is related to the stability of these nanoparticles during the continuous heating (growth, coarsening, or dissolution) and cooling (reprecipitation) conditions of welding as well as during post-weld treatments. Strength loss is often observed in the fusion and heat-affected zones of low-carbon steels due to the dissolution of nanoparticles during the weld heating. Generally, there are two commonly used methods for strength recovery. One is to use post-weld heat treatment to induce the re-precipitation of nanoparticles and reestablish the strength [78]. For example, the recovery of the strength and ductility in the fusion and heat-affected zones of an NiAl/Cu co-precipitation-strengthened steel can be achieved after annealing at 600°C for 30 min [79]. However, the post-weld heat treatment is not feasible for many large-scale engineering applications such as naval ship structures because of the size and complexity of the structures. Alternatively, the strength recovery in the HAZ could be achieved by designing an appropriate multi-pass welding procedure that leads to similar reprecipitation during the postweld heat treatment. Yu et al. investigated the effects of multi-pass welding on the evolution of Cu nanoparticles in BA160 steel, a low-carbon steel strengthened primarily by bcc-Cu and (Mo,Cr,V)2C nanoparticles [80]. An atom map of Cu in the single-pass HAZ of the BA-160 sample is displayed in Fig. 8a. The Cu atoms are homogeneously distributed, and no Cu-enriched clusters are observed in the single-pass HAZ, indicating that almost all pre-existing Cu nanoparticles are dissolved in the matrix during the single-pass weld cycle. A subsequent second-pass welding with a peak temperature of 650°C triggers the reprecipitation of Cu nanoparticles. As illustrated in Fig. 8b, a high number density of Cu nanoparticles with an average radius of 2.6 nm can be readily detected [80]. In addition, the Cu concentration in the matrix decreases from 2.86 to 0.85 at.% after the second-pass welding, further confirming that the reprecipitation reaction occurs during the second thermal cycle. Furthermore, the (Mo,Cr,V)2C carbides that are dissolved into the matrix during the first-pass welding also reprecipitate out after the second-pass welding, similar to the behavior of Cu precipitates [80]. The microhardness of the single-pass HAZ is about 340 HV, which is much smaller than that of the as-received base metal, 402 HV. For double-pass HAZ samples, the microhardness is approximately 405 HV, indicating strength recovery by double-pass thermal cycles [80]. The above results demonstrate that the multi-pass welding method is applicable and effective in joining the nanoparticles strengthened steels without significant loss of strength in the HAZ.

Irradiation resistance

The long-term stability of structural steels in highly irradiated environments is a critical issue for future generations of advanced reactors and related technologies [81]. Upon neutron irradiation in nuclear plants, many steels exhibit radiation-enhanced hardening and embrittlement, because radiation-enhanced generation and diffusion of point defects and solute atoms accelerates the formation of high densities of nanoscale precipitates such as Cu-enriched nanoclusters [82]. On the contrary, ODS steels containing high densities of pre-existing oxide nanoclusters can manifest excellent radiation tolerance due to the recombination of irradiation-induced defects by these stable nanoclusters [83]. Because of the high cost and engineering difficulty in processing ODS steels, it is technologically important to understand the stability of other types of pre-existing precipitates under irradiation and their effects.
on radiation-induced defects. The effect of pre-existing Cu nanoparticles on irradiation resistance of a Fe–2.5Cu–4Ni–1.5Mn–1Al steel was studied by APT and hardness tests [38]. Pre-existing Cu nanoparticles were formed by aging the steel at 500°C for 10 h. Atom maps of Cu, Ni, Al, and Mn of the aged steel before irradiation are shown in Fig. 9a [38]. Cu nanoparticles enriched in Cu, Ni, Al, and Mn have an average size of 1.7 nm and number density of $1.1 \times 10^{24} \text{ m}^{-3}$. After irradiation (Fig. 9b), the precipitate size increases to 2.1 nm, while the number density decreases to $6.4 \times 10^{23} \text{ m}^{-3}$ [38]. A slight decrease in the concentration of Cu in the matrix from 0.32 to 0.22 at.% is also observed after irradiation. In addition, the hardness of the steel containing pre-existing Cu-rich precipitates decreases from 6.0 to 5.2 GPa after irradiation, indicating radiation-induced softening, rather than hardening. According to the theory of precipitate stability under irradiation, precipitates can grow through the diffusion of solutes or solute clusters in the matrix or can shrink due to radiation-induced recoils and ballistic ejection of precipitates [84]. The above results demonstrate that pre-existing Cu precipitates do not dissolve into the matrix but coarsen during irradiation, which is responsible for the decrease in hardness after irradiation. These results indicate that pre-existing Cu nanoparticles are not the dominant factor inducing embrittlement. In contrast, these pre-existing nanoparticles in steels can be sinks for both vacancy and interstitial point defects, and hence can act as recombination centers under irradiation conditions. Therefore, Cu nanoparticles appear to enhance the radiation resistance of steels.

**Future work**

To further speed up the development of new nanoscale co-precipitation-strengthened steels and promote their wide industrial applications, future efforts should be focused on the comprehensive understanding of the composition-processing-microstructure-property relationship of this class of nanostructured steels and the improvement of their overall properties for various applications.

**Low-temperature toughness – an important issue for all ultra-high strength steels**

Low-temperature toughness is one of the major mechanical properties of structural steels. It has been found that toughness is sensitive to the microstructure of steels, including precipitate microstructure, grain size, and grain boundary chemistry, which, in turn, is determined by the alloy composition and processing conditions [85,86]. Previous studies indicate that Cu-strengthened steels such as the NUCu-140 steel exhibit a good combination of high strength and high toughness at low temperatures, which is considered to be attributed to a possible reduction of the local Peierls stress in the matrix by the small misfitting Cu nanoparticles [25,29]. On the contrary, many high-strength steels suffer from temper embrittlement as evidenced by a sharp decrease in toughness when tempered at 400–550°C [87]. To date, there has been little systematic analysis on the low-temperature toughness of nanoscale co-precipitation-strengthened steels. Therefore, it is important to understand the key factors governing the low-temperature toughness of nanoscale co-precipitation-strengthened steels.
steels and to develop advanced steels with a good combination of high strength and high toughness for industrial applications.

**Stability of various nanoparticles in steels at elevated temperatures**

Thermal stability of nanoparticles is important for elevated-temperature applications of the steels because strength degrades when particles become coarser. Interestingly, some particles such as Ni/Al/Ni2AlTi are stable at elevated temperatures, indicating the feasibility to develop highly stable nanosized particles. In previous studies, the focus was mostly placed on the nucleation and growth mechanism of the nanoscale co-precipitates, and there has been a lack of a careful study and full understanding of their coarsening behavior. It is known that particle coarsening kinetics can be affected by many factors such as the volume fraction of nanoparticles, elastic strain due to the particle/matrix mismatch, elastic interaction between the particles, loss of coherency, and surface energy of precipitates [88]. The coarsening behavior of nanoscale co-precipitates becomes more complex because synergistic alloying effects and the co-precipitate interaction may have a significant impact on the elastic and surface energies of the nanoparticles. Thus, it is of both fundamental and technological importance to critically investigate the coarsening kinetics and thermal stability of nanoscale co-precipitates at elevated temperatures.

**Micro-mechanical properties of nanoparticles and their correlation with bulk steel properties**

It is known that the strengthening efficiency of nanoparticles depends highly upon the nature of dislocation interaction with the nanoparticles, which is essentially controlled by the intrinsic micro-mechanical properties of the nanoparticles. However, because of their small size (~10 nm or below), which is too small for most conventional mechanical techniques, their micro-mechanical properties are seldom reported. Moreover, some nanoscale co-precipitates may undergo complicated structural and/or microstructural transformations. For example, Ni/Al/Ni2AlTi co-precipitates exhibit a hierarchical structure with the Ni2AlTi substrates forming within the primary NiAl particles [42,43,69]. Another example is the Cu nanoparticles, which exhibit a unique structural evolution with aging time, i.e., bcc Cu → 9R hexagonal Cu → fcc Cu [28–40,54–62]. It has been considered that the strengthening effect of complex nanoscale co-precipitates may be related to their unique microstructures and micro-mechanical properties. Thus, future attention needs to be directed toward assessing the micro-mechanical properties of these nanoscale co-precipitates and correlating them with bulk steel properties.

**Concluding remarks**

This review highlights recent advances in alloy design, nanostructural characterization, and unique properties of nanoscale co-precipitation-strengthened steels, with an emphasis on composition-processing-microstructure-property relationship in this class of nanostructured steels. Alloy design of these steels is now increasingly oriented toward the integrated computational-prediction and experimental-validation approach. Computational techniques such as Thermo-Calc and DFT first-principles calculations provide useful guidelines for alloy design, and state-of-the-art analytical tools such as APT and Cs-TEM enable the detailed observation of nanostructures and quantitative analysis. In particular, APT can determine the composition and morphology of nanoparticles less than 1 nm in size. There have been a number of successful developments of ultra-high-strength steels strengthened by multiple types of nanoparticles, including bcc-Cu, B2-NiAl, L21-Ni3AlMn and Ni3AlTi, η-Ni3Ti, NbC, and M23C. The synergistic combination of these nanoparticles plays an important role in determining the bulk properties of the steels, including the mechanical, welding, and irradiation properties. To further speed up the development of new nanoscale co-precipitation-strengthened steels and promote their wide industrial applications, future work should be focused on the improvement of the impact toughness at low temperatures and the thermal stability at elevated temperatures as well as the correlation between the micro-mechanical properties of the incorporated nanoparticles and bulk steel properties.

**Acknowledgements**

This research was supported by the internal funding from the City University of Hong Kong (account no. CityU 9380060), General Research Fund (account no. CityU 11205515) and Collaborative Research Fund (account no. C1027-14E) from the Research Grants Council, Hong Kong. MKM and atom probe tomography research were supported through a user project funded by ORNL’s Center for Nanophase Materials Sciences (CNMS), which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

**References**
