REVIEW

On the role of transmission electron microscopy for precipitation analysis in metallic materials

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ABSTRACT
Precipitation hardening is one of the most important strengthening mechanisms in metallic materials, and thus, controlling precipitation is often critical in optimizing mechanical performance. Also other performance requirements such as functional and degradation properties are critically depending on precipitation. Control of precipitation in metallic materials is, thus, vital, and the approach presently in the limelight for this purpose is an integrated approach of theory, computations and experimental characterization. An empirical understanding is essential to build physical models upon and, furthermore, quantitative experimental data is needed to build databases and to calibrate the models. The most versatile tool for precipitation characterization is the transmission electron microscope (TEM). The TEM has sufficient resolving power to image even the finest precipitates, and with TEM-based microanalysis, overall quantitative data such as particle size distribution, volume fraction and number density of particles can be gathered. Moreover, details of precipitate structure, morphology and chemistry, can be revealed. TEM-based postmortem and in situ analysis of precipitation has made significant progress over the last decade, largely stimulated by the widespread application of aberration corrected microscopes and accompanying novel analytics. The purpose of this report is to review these recent developments in precipitation analysis methodology, including sample preparation. Application examples are provided for precipitation analysis in metals, and future prospects are discussed.

KEYWORDS
Precipitation; transmission electron microscopy; precipitation hardening; phase transformation; metallic materials

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1. Introduction

Precipitation hardening generating an increased hardness and/or strength of an alloy due to fine particles precipitated upon aging of a supersaturated solid solution was discovered by Wilm \cite{1} and commercially introduced under the trade-name Duralumin in the beginning of the twentieth century. \cite{2,3} Merica et al. \cite{4} provided an early explanation of the phenomenon but it took roughly 30 years from the discovery of the effect before its microstructural origin, i.e., Guinier–Preston (GP) zones, could be identified by utilizing small-angle X-ray scattering (SAXS). Since then, a lot of attention has been directed toward precipitation and precipitation hardening. Early on, the precipitation analysis was mainly conducted through X-ray techniques using single crystals \cite{5} and the advancement for steels was falling behind the lightweight alloys, since it was more difficult to prepare single crystalline steels. The understanding of precipitation took a leap when the application of transmission electron microscopy (TEM, the acronym is used interchangeably for microscope and microscopy) became more widespread in the 1940s. Precipitation analysis in steels became more tractable and, for example, coarser precipitates were analyzed by TEM on extraction replica samples. \cite{6} Over the years, sample preparation techniques and instrumentation have made significant advances, which have helped to solve the early struggles. Nowadays, TEM is one of the few techniques capable of resolving nanoscale precipitates and dislocation–precipitate interactions \cite{7}; and, about one century after the discovery by Wilm, it is clear that TEM contributes significantly to the development of precipitation engineered high-performance alloys. Recent examples where TEM has contributed to precipitation engineering in alloys are: high-angle annular dark field (HAADF) technique has accelerated the development of advanced ultra-high strength alloys through understanding of coherency and misfit of nanoscale B2 ordered precipitate phase in Fe–Ni–Al–Mn alloys \cite{8}; a combination of HAADF, electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS) has revealed the Cu core-B2 Ni(Al, Mn) shell structure in high-performance Fe–Cu–Mn–Ni–Al alloys \cite{9}; in situ TEM has improved the knowledge of precipitate–dislocation interactions in Al–Mg–Sc alloys at elevated temperatures in real time. \cite{10}

The recent focus on enhanced materials innovation rates by reducing the development and implementation time puts emphasis on computational methods. \cite{11,12} Integrated computational materials engineering (ICME) \cite{13,14} and integrated computational materials design (ICMD) \cite{15,16} are important concepts in this work. A mature ICME/ICMD framework would facilitate the transition from traditional materials discovery into an efficient, computationally driven design process. In such a framework, advanced experimental tools are key technology drivers. Experimental tools and methods are needed to build mechanistic understanding upon which models can be based but the tools are also needed to acquire data for building databases and calibrating models. In fact, advanced methods allowing for three-dimensional (3D) and in situ characterization are becoming more important today due to the advancement of the modeling. For instance, precipitation modeling by the Langer–Schwartz–Kampmann–Wagner (LSKW) approach \cite{17–20} needs 3D experimental information of particle size distribution and property modeling is nowadays capable of treating the full 3D microstructure. \cite{21} Specifically for precipitation, high-resolution techniques capable of resolving nanoscale precipitates with proper statistics are needed. 3D and in situ capabilities provide added benefits. Tools currently used to characterize precipitates are TEM, atom probe tomography (APT) \cite{22,23} and small-angle scattering (SAS). \cite{24–27} TEM is the most versatile out of these tools for precipitation characterization and it is capable of quantitatively characterizing, for example, structure, chemistry, morphology and dispersion of precipitates. \cite{28} By measuring and controlling these precipitation parameters, it is possible to tune and optimize properties of the material, not only the more standard mechanical properties such as strength and ductility but also creep resistance, \cite{29,30} wear resistance, \cite{31} functional \cite{32} and degradation \cite{33,34} properties (see schematic illustration in Figure 1).

TEM-based analysis has made significant advances during the last decade with more widespread implementation of aberration corrected microscopes and improved analytic instrumentation as well as novel methods to fully
benefit from the capabilities of these prime microscopes, see examples in Refs. [35–38]. Current TEM capabilities are even expanding toward nanoscale laboratories where structures are assembled atom by atom.[39–41] Being such an important technique in materials science, TEM capabilities have been reviewed on multiple occasions recently.[42–46] However, though TEM is key in the field of precipitation in metallic materials,[2,47–50] there has been no recent effort to elucidate the current capabilities of TEM-based analysis of precipitation in metallic materials. We aim to make such an effort in the present report. The recent developments of TEM capabilities that have bearing on precipitation analysis in metallic materials are reviewed and application examples are provided. Furthermore, an outlook on future prospects in the field is given. The structure of the report is the following. After this introductory section: Section 2 describes sample preparation methodologies for precipitation analysis in TEM; Section 3 describes the state-of-the-art in TEM methodology for precipitation analysis; Section 4 gives recent application examples for precipitation analysis in metals; Section 5 provides the authors’ viewpoints on existing challenges and opportunities; and, finally, the report is concluded with a summary (Section 6).

2. Sample preparation for analysis of precipitation

Samples for TEM analysis have stringent requirements of electron transparency, extreme thinness for

Figure 1. A schematic illustrating the plethora of TEM capabilities for analyzing precipitate characteristics, of importance for various properties of metallic materials. (Abbreviations in the figure: Deform: Deformation; Concentration; Orient: Orientation; Tomo: Tomography; Spect: Spectroscopy; Diff: Diffraction; Imag: Imaging).
optimized high-resolution analysis, contamination avoidance, artifact free, etc. When preparing these samples from bulk materials, it is clearly important to make sure they are representative of the bulk material and also to avoid relaxing or introducing strains and stresses.\[51\] Since these requirements are complicated to meet, sample preparation is a critical step for successful TEM analysis. Therefore, various sample preparation techniques for precipitation analysis are elucidated here, and the advantages and disadvantages of these techniques are summarized in Table 1.

### 2.1. Thin-foil preparation

Thin-foils are most widely used for TEM characterization of bulk metallic materials as well as precipitates therein. In the case when bulk information about precipitates forming well-dispersed in the microstructure is desired or large area of interest for good statistics is required, thin-foil specimen prepared by twin-jet electro-polishing method is the most efficient. The general procedures for preparing thin foils from bulk metal samples are\[51,52\]: (i) cutting the bulk material into approximately 0.3–0.5 mm thickness slices, grinding and polishing on different grade silicon carbide papers to approximately 50–200 μm thickness, while ensuring that the damaged layer can be fully removed in the subsequent electro-polishing; (ii) punching out 3 mm-diameter disks; (iii) finally twin-jet electro-polishing using appropriate conditions for the studied material, i.e., proper electrolyte, voltage and temperature in a dedicated electro-polishing equipment, for instance, a Struers Tenupol-5 or Fischione 110 polisher (the procedure is shown schematically in Figure 2a).

In some cases, other techniques may be preferred for specimen preparation to study precipitation in bulk metallic materials. For example, in materials such as hard metal composites and multiphase materials where it is hard to get a sufficiently large uniform thin area due to differential thinning in the electro-
polishing method,[51] an alternative way is to use a combination of dimple grinding and precision ion-polishing.[53] Another alternative method for these difficult materials is to electro-polish to form a perforation, followed by broad ion beam (BIB) milling and polishing to obtain a uniform thin area, thus, minimizing the artifacts arising due to differential thinning.[54] For ion polishing, parameters including voltage, angle and rotation rate are usually tuned to minimize defects associated with the preparation.[55] For final cleaning of TEM samples that were made by different preparation techniques, plasma cleaning is often used to remove contaminations, such as hydrocarbon and carbonaceous compounds before the thin-foil is inserted into the TEM chamber. Depending on the specifics of plasma cleaning, a blended oxygen/argon process gas or pure argon or oxygen can be used.[56,57]

### 2.2. Site-specific bulk preparation

When specific regions in the bulk material are of interest (e.g., studies of precipitates nucleated at various defects), or when accurate control of specimen thickness is needed (e.g., studies of chemistry around precipitate–matrix interface), focused ion beam (FIB) is the primary specimen preparation method of choice.[58–61] The specimen preparation by FIB is usually conducted in an electron-ion instrument equipped with two beam columns, i.e., one focused beam of electrons for imaging and one focused beam of ions for sputtering or milling/polishing. The procedure for TEM thin foil preparation by FIB includes: (i) depositing a first protection layer (normally Pt) on the area of interest (AOI), (ii) peripheral and bottom cutting around the AOI but leaving a micro-bridge connecting the AOI and the bulk material, (iii) fixing the micromanipulator probe, to be used in the extraction of the sample, to the sample by deposition before the final cutting of the micro-bridge and (iv) transferring the sample using the micromanipulator to a TEM grid and fixing it to the grid by deposition (see Figure 2b). Using FIB, thin foil TEM specimens can either be prepared perpendicular or parallel (plan–view lift-out) to the sample surface.[62] With the development of the FIB technology, there are currently many possible ion beam chemistries and source types available either commercially or in the research prototyping phase. For example, gas (e.g., He⁺ and Ne⁺) field ionization sources (GFIS), inductively coupled (e.g., Ar⁺ and Xe⁺) plasma (ICP), liquid metal (e.g., Ga⁺) and alloy ion sources (LMAISs) and laser-cooled low temperature ion sources (LoTIS) have been applied frequently.[63,64] The most common ions that are used in commercial FIB instruments are He⁺, Ne⁺, Ar⁺, Ga⁺ and Xe⁺, which enable milling and imaging at length scales over several orders of magnitude (1 nm to 1 mm) by offering a large range of available ion currents, energies and beam sizes.[63] For more details of the theory, ion–solid interactions, applications, advantages and limitations of different ion sources, see Refs. [63–65].

Despite the aforementioned advantages as compared with, e.g., electro-polishing, FIB has a major disadvantage when it comes to materials characterization, e.g., precipitate analysis at a high-resolution atomic scale – beam damage. The energetically implanted ions leave a damaged zone under the target area that can alter the chemistry and structure of materials, but it varies with ion beam source, employed material and working condition.[62,66] For example, the implantation of Ga⁺ can lead to its chemical interaction with materials which are chemically sensitive to Ga⁺, e.g., Cu containing materials can form intermetallic phase Cu₃Ga.[67] However, with the use of an ion source consisting of Xe⁺ or Ar⁺, the chemical reactions are prevented due to the noble nature of the gas. In addition, the material can undergo a crystalline-to-amorphous/phase transition when the number of accumulated defects or the critical amount of deposited energy exceeds a threshold value.[68–73] To minimize the heating induced artifacts due to continuous transfer of kinetic energy of ions to the target materials, either cooling the specimen using a liquid nitrogen stage, or employing the ion beam modulation feature in which the sample is not exposed to the ion beam continuously, is applied.[74] The reduction of ion energy (accelerating voltage below 2 keV) and milling angles, for bulk specimen milling, minimizes ion beam damage, formation of amorphous layer and specimen heating, and low angles of incidence facilitate uniform thinning of dissimilar materials.[63,75,76] Therefore, a low-energy cleaning step is particularly important in preparation of high-quality samples.[63,74] To find an efficient approach that can consistently remove defects produced by FIB, a flash electropolishing approach was first reported by Ando et al.[77] By electropolishing for a very short time (~0.2 s), a surface damage layer (~20 nm) could be completely removed in Fe-Ni-Cr alloys.[77] Later on, such a flash electropolishing approach has been used to remove the damaged layer to produce high quality TEM specimens for oxide dispersion strengthened alloys,[78] ultra-high purity iron,[79] and neutron/ion irradiated ferritic alloy.[80]
etc. By this approach, the nanoscale precipitates and neutron/ion irradiation-induced defects in the irradiated materials are possible to characterize accurately. Another possible solution to the FIB damage is the utilization of low acceleration voltage and low incident beam Argon ion milling in the new generation of three-beam microscopes, which has been proven to be an effective technique to prepare high quality lamellae of metallic materials. In addition, similar as described for bulk thin foils earlier, a combination of FIB-based lift-out technique with post-processing in BIB has been also proposed to minimize or eliminate this damage and ensure high quality analysis results. This combination is particularly useful since only the most advanced FIB systems are capable of reducing the ion energy below 2 keV using energetic Ga\(^\text{+}\) ions. An additional advantage of combining these two techniques is the reduction of specimen preparation time. For more details of various FIB TEM specimen preparation techniques, see Refs. [51,60–64,83].

### 2.3. Chemical extraction

The preparation of extraction replica is a traditional but important sample preparation methodology for the study of precipitates, nonmetallic inclusions and microstructures in different kinds of materials. The extraction replica samples are usually prepared by first grinding, polishing and slightly etching the bulk sample, before a replica foil such as carbon of approximately 20 nm thickness is deposited on the etched surface using a coating instrument, e.g., Gatan 682 PECS\(^\text{TM}\) (precision etching and coating system). Thereafter, the coated film is cut into approximately 2 \(\times\) 2 mm\(^2\) grids by a razor blade and then these smaller films are floated off in an etchant suitable for the studied material, utilizing either electro-etching or chemical etching. The coated films are cleaned by ethanol multiple times and unfolded in a mixture of distilled water and ethanol. Finally, they are collected on a support grid of, e.g., Cu or Mo and dried thoroughly (see Figure 2c). Depending on the nature of the material and what should be analyzed, various coatings such as Al, Au, Au/Pt, Ag, Cr, Ti can be used. Carbon coating is the prevailing coating for steels, where an amorphous coating consisting of a light element that provides a large mean free path of the electrons is preferred.

In comparison with the aforementioned thin-foil TEM samples, the extraction replicas for the precipitate analysis have the following benefits: (i) elimination of the influence of the matrix during chemical and diffraction analyses of precipitates, (ii) increase of the contrast between the particles of interest and the background during TEM imaging, (iii) increase of the concentration of alloying elements within the precipitation process with a continuous evolution of the size of \(\text{M}_6\text{C}\) in steels. This evolution could increase or decrease the chemical resistance of the precipitates, which leads to the dissolution of precipitates in concentrated acid solutions, which are usually applied in the chemical extraction process. Hence, electrochemical dissolution could be a better choice in certain cases. This is because it can be easier to control the type of dissolving phase and its electrochemical dissolution rate by applying an electrochemical potential. The consequence is that fine precipitates are less likely to be dissolved during sample preparation using electrolytic extraction as compared to chemical extraction sample preparation. The main control parameters during electrolytic extraction are: the electrolyte used, voltage, current density, temperature and time. Moreover, the subsequent treatments

### 2.4. Electrolytic extraction

In addition to the thin-foils and chemical extraction replicas, electrolytic extraction is another method to prepare TEM samples in order to obtain quantitative information of precipitates in bulk materials. This method is based on an electrochemical procedure, selectively dissolving the steel matrix and separating the undissolved particles from the matrix by filtration. The filtered precipitates are then used for the preparation of TEM samples in a similar way as for nanosized powder materials (see Figure 2d). The aforementioned chemical extraction is a relatively simple method to separate highly chemically resistant precipitates from the matrix. However, the chemical resistance of precipitates may change during the precipitation process with a continuous evolution of the concentration of alloying elements within the precipitates, e.g., Cr concentration increases with the size of \(\text{M}_6\text{C}\) in steel. This evolution could increase or decrease the chemical resistance of the precipitates, which leads to the dissolution of precipitates in concentrated acid solutions, which are usually applied in the chemical extraction process. Hence, electrochemical dissolution could be a better choice in certain cases. This is because it can be easier to control the type of dissolving phase and its electrochemical dissolution rate by applying an electrochemical potential. The consequence is that fine precipitates are less likely to be dissolved during sample preparation using electrolytic extraction as compared to chemical extraction sample preparation. The main control parameters during electrolytic extraction are: the electrolyte used, voltage, current density, temperature and time.
of the residues after the particles have been separated from the bulk matrix are important, and precipitates with size down to 5–15 nm could be successfully collected due to electrostatic attraction effects.\cite{98,99,103} The major challenges here are to find a proper electrolyte and the applied electrochemical potential that selectively dissolve the matrix rapidly without dissolving the precipitates. In addition, the possibility to dissolve large volumes of the bulk material makes electrolytic extraction advantageous in studying precipitate volume fraction and identification of multiple precipitate phases by combining with X-ray diffraction (XRD).\cite{103,106}

3. TEM-based methods for precipitation analysis

Even though the focus of this work deals with TEM characterization of nanoscale precipitates in metallic materials, it has to be mentioned that SEM is always recommended beforehand, especially for relatively large precipitates, considering the advantages of SEM with easier sample preparation with less possible artifacts and that they are readily available in materials laboratories. Moreover, SEM has good resolution down to about 10 nm for typical precipitates in metals, and provides the possibility to perform 3D-FIB tomography analysis,\cite{107} electron backscatter diffraction (EBSD) and transmission Kikuchi diffraction (TKD) for crystallographic analysis.\cite{108} Furthermore, the large chamber space aids in situ analysis and the development of low voltage EDS analysis in SEM should also be mentioned, since it can readily provide chemical analysis with spatial resolution down to a few tens of nanometers.\cite{109}

TEM-based analysis of precipitates deals with two basic goals – first is the identification of the precipitate(s) type and second is the quantification of the precipitates. A full determination of the character of the precipitate requires both diffraction and chemical data. There are also other important features related to precipitates such as misfit of precipitate–matrix interfaces\cite{110}; the identification of misfit aids misfit strain analysis that in turn affects the dislocation motion, and thus, strength of the material. A full quantification of precipitates requires TEM analysis based on imaging, diffraction, spectroscopy and tomography methods.

TEM-based techniques can be divided broadly into three categories – imaging, diffraction and spectroscopy. Conventionally, diffraction-contrast-based imaging techniques such as bright field (BF) and dark field (DF) imaging are widely used in characterizing and quantifying precipitates.\cite{111} They are also combined with other complementary techniques such as convergent electron beam diffraction (CBED) and electron energy loss spectroscopy (EELS) techniques for advanced analysis of precipitate crystallography, composition and chemical states. Additionally these methods provide localized sample thickness measurements in order to perform volume-based quantification of precipitates.\cite{112–115} The combination of BF/DF imaging with energy dispersive X-ray spectroscopy (EDS) has provided an opportunity for efficient characterization of precipitates in metallic systems.\cite{95} With scanning possibilities in TEM, the conventional scanning TEM (STEM)-based imaging techniques such as annular dark field (ADF), high-angle annular dark field (HAADF) and BF imaging provide conditions with removal of artifacts, such as bend contours that are caused by the occurrence of high-order diffraction when a particular set of diffracting planes is not parallel everywhere.\cite{116}

The novel developments of TEM, such as chromatic aberration correction (Cc) and spherical aberration correction (Cs), significantly improve the signal-to-noise ratio and achieve a sub-Ångström spatial resolution due to the improved focus of electrons of different wavelength and the reduction in energy spread of electrons and point spread arising from the refraction power of a real lens that increases with the angle between the entering beam and the instrument’s optical axis.\cite{117–120} Optionally, the increased accelerating voltage can also aid attaining higher resolution due to lowering of electron wavelength. An example of the application of high accelerating voltage and double Cs correction can be seen in Figure 3,\cite{121} where Cs aberration correction was applied to both probe and image formation lenses. Dramatic improvement in resolution is achieved with an excellent imaging of atomic arrangements within the chemically ordered precipitate and its lattice coherency with the matrix. Except for STEM-HAADF,\cite{122,123} the capability of TEM-based techniques like in situ characterization\cite{124,125} and atomically resolved STEM-EDS/EELS\cite{126–128} are improved or achieved. Among these advanced techniques, atomic-resolution STEM-HAADF imaging technique in Cs- or/and Cc-corrected TEM, combining with EDS and EELS, has become a mainstay in recent years for characterization of precipitates with size in the order of only a few nanometers.\cite{9,129–131} Starting with these high-resolution imaging and spectroscopy techniques, the
3.1. High-resolution imaging

High-resolution imaging techniques include high-resolution TEM (HRTEM) and high-resolution STEM-HAADF, -BF, -ADF imaging. By using the elastic interaction of a coherent parallel electron beam in conventional TEM mode with the crystal lattice forming an interference pattern (phase contrast), HRTEM is an efficient technique to study the atomic scale structure of precipitates. Before imaging, the grains or crystals require accurate tilting to align atomic columns with a low index zone axis along the electron beam direction to achieve good atomic resolution in the imaging plane. HRTEM imaging together with fast Fourier transformation (FFT) analysis can be applied for structural determination of fine precipitates, whereas diffraction intensity from a very small volume is limited for the SAED method. By collecting the transmitted scattered electrons with a high-angle annular detector after the interaction of a convergent beam in STEM mode with precisely aligned atomic columns in the region of interest, HAADF can provide chemically sensitive information (Z-contrast) that helps distinguishing individual intensity variations in the atom columns and the chemistry related to atom positions in the crystal structure.

Therefore, HAADF shows benefits over HRTEM for studies of elemental distribution within fine precipitates. Energy filtering (EF) is another step forward in the TEM imaging, with atomic resolution. This utilizes the electron energy loss spectrum for formation of elemental images through introduction of energy selecting slits in two window jump ratio method, three window method and chemical state mapping from the characteristic energy loss edges corresponding to individual chemical elements and the profile variations due to electronic states. The benefits of EF include contrast enhancement through removal of inelastically scattered electrons while imaging, and characteristic EFTEM mapping for quantification of precipitate phases based on their chemistry.

3.2. Spectroscopy

Spectroscopy techniques include EELS and EDS. EELS works on the principle of identification and separation of inelastically scattered electrons of different energy that have transmitted through the specimen after interactions with the sample material, resulting in a spectrum of electron intensity against the energy lost in the interaction. Whereas EDS works on the principle of detecting characteristic X-rays which are emitted from different elements in the material after the electron–atom interaction. These two techniques are complementary to each other, but it is noteworthy that EELS has higher requirements on sample thickness as compared to EDS. EELS has its strength on analysis of low-Z elements and identifying the differences in electronic states of the element in the compounds (e.g., precipitates) through analysis of core-loss edges utilizing multiple proposed methods such as white-line ratio, chemical shift, energy-loss near-edge structure (ELNES) fitting, etc. Different parts of the EELS spectrum such as the low-loss spectrum, Plasmon peaks and core-loss edge and near-edge spectroscopy can be used to analyze various material characteristics. For example, the low-loss spectra, which is also called valence electron energy loss spectra, contains information about defects and interfaces with atomic scale resolution, these analysis must, however, be performed with caution since spatial resolution is limited by the delocalization of the EELS signal. ELNES, for example, provides information about the electronic and atomic environments around an intended atom species, similar to the X-ray absorption near-edge structures. ELNES is particularly useful in the chemical analysis of light elements in very small
precipitates, e.g., carbon content in carbides, through combining with extraction replica and plasma cleaning.\textsuperscript{[146]} In the case of EDS, it applies mostly to high-Z elements. With the introduction of windowless and solid state detectors such as silicon drift detectors, low-Z elements can also be identified, while quantification is still an issue for some ambiguous elements such as C, due to other sources of contamination in the sample as well as in the TEM chamber (The same issue exists for EELS analysis as well). With the introduction of multiple EDS detectors which enhance the collection efficiency through a large collection area, the EDS scenario has been improved in TEM.\textsuperscript{[147]} Within a relatively short time, high resolution EDS spectral maps can be obtained, without the need of tilting the sample to improve detection, which was the case in conventional systems with only one EDS detector working with a tilttable specimen holder. The introduction of wavelength dispersive spectroscopy (WDS) as used in SEM for the quantification of low-Z elements was not considered to be efficient due to space limitation within the S/STEM column.\textsuperscript{[101,148]} Wavelength dispersive soft X-ray emission spectroscopy within TEM has been developed in the past decade, which has potential for analyzing density of states and bonding characters of nanometer scale features.\textsuperscript{[149,150]}

3.3. Diffraction

In the identification and accurate analysis of crystallographic information, SAED, nanobeam diffraction (NBD) and CBED have been offering promising solutions. SAED is formed by a parallel beam of electrons, whereas in NBD and CBED the beam is converged, the convergence angle being smaller for NBD than CBED. SAED patterns are usually spot patterns or ring patterns depending on the size of crystal and the aperture used. While SAED is limited by the aperture size for selecting region of interest, particularly for nanoscale precipitates, it enables the formation of bright and dark field images with controlled diffraction conditions.\textsuperscript{[101]} NBD enables formation of diffraction patterns from a nanoscale region of the sample, but the diffraction pattern will consist of disks instead of spots as in the SAED. With increase in convergence angle from the stationary nanobeam, CBED technique results in Kossel patterns which can provide detailed information about the crystal structure of the precipitates.\textsuperscript{[151,152]} Compared to the above diffraction methods, precession electron diffraction (PED) is a non-stationary beam that is tilted and made to precess over a predefined surface of a cone, the angle of which is variable. This technique provides more reliable interpretation of the diffraction pattern since the precession reduces the nonsystematic dynamical effects and improves interception of the Ewald sphere.\textsuperscript{[153]} Automated crystal orientation mapping (ACOM-TEM) using the PED technique enables automatic mapping in TEM, similar to EBSD, but with resolutions of up to 1–3 nm when a field emission electron gun (FEG) is used. It is a high-end technique for orientation mapping and phase identification of nanoscale precipitates,\textsuperscript{[154–156]} its potential widespread use is expanded in Subsection 5.3.

3.4. In situ methods

Conventional \textit{ex situ} characterization of precipitates in materials at room temperature is inevitably affected by factors such as stability of the precipitates during cooling and ambiguity in temperature of initiation of precipitation, since all examinations are performed post mortem at room temperature. Additionally, there are unknown factors of influence such as thermal stresses and their effect on precipitates during cooling (e.g., elastic strain-induced bcc-to-9R structural transformation in Cu precipitates\textsuperscript{[157]}), and artifacts introduced through mechanical strain during sample preparation. \textit{In situ} heating and cooling in TEM possibly avoid these factors and enable monitoring of the precipitation process, and moreover, the effect of other environments such as radiation, deformation, etc. can be studied.\textsuperscript{[123–125,158,159]} The possible applications could include but are not limited to: \textit{in situ} studies of nucleation-growth-coarsening,\textsuperscript{[158–162]} precipitate impingement,\textsuperscript{[163]} precipitate splitting (reverse coarsening),\textsuperscript{[164]} precipitation under irradiation,\textsuperscript{[165]} structural transformation of precipitates during heat treatment or deformation,\textsuperscript{[95]} and precipitate–dislocation interaction.\textsuperscript{[10,166,167]} All these fields are promising but still in their rudimentary stages. \textit{In situ} TEM sample holders that perform heating have been in development and in use for many decades. Recently micro-electro-mechanical systems (MEMS)-based heating and cooling holders with precise control over the rate of heating/cooling have become widely used.\textsuperscript{[168]} \textit{In situ} sample stages also offer wide possibilities of deformation to study the interaction of defects with microstructural features such as precipitates.\textsuperscript{[169]}

3.5. Tomography

3D tomography, as a technique which derives 3D information from 2D images, is invaluable in analyses of morphology and interconnectivity of precipitates.\textsuperscript{[170,171]} The 3D electron tomography (ET)
conventionally applies the diffraction contrast for imaging, while advances in EDS (such as multiple detectors with high collection angle and efficiency) and EELS (such as the improvements in Gatan Imaging Filter) have enabled the use of EDS and EELS signals for 3D tomography as well.\cite{172–175} Use of needle shaped samples instead of thin foils avoids projected thickness variations during tilting. This method suits well for the precipitates of size range less than 100 nm.\cite{176} In addition, atomic resolution technique, can provide 3D information of nanoparticles within a matrix,\cite{177–180} but it is very challenging for embedded particles where different elements are mixed. For a complete understanding of nanoscale precipitates in 3D, correlative ET-APT presents an unprecedented opportunity. The two techniques are complementary to each other, as ET provides larger-scale morphological information and APT provides smaller-scale chemical information. This combination also allows for the detection of artifacts, the determination of optimal reconstruction parameters, the evaluation of the reconstruction quality, etc., associated with both techniques.\cite{181} It is noteworthy that ET is nondestructive while APT is a destructive method.

3.6. Miscellaneous methods

It should also be mentioned that the usage of Moiré fringes-based techniques for identifying the crystal structure of precipitates and other nanoscale features can also be very useful, as demonstrated in NiAl and aluminum alloys in the literature.\cite{182,183} The same technique could readily also be employed in the identification of other precipitate types in metallic materials. The technique is based on the interference patterns that are generated due to the overlapping patterns of precipitate and matrix, see the details in Ref. [182]. Another interesting technique is electron holography. It is a powerful technique for mapping electrostatic and magnetic fields in nanoscale structures, and its application for studies of the electric and magnetic nature of nanoprecipitates\cite{184,185} and interfaces\cite{186} has been demonstrated.

4. Precipitation engineering in metals aided by TEM analysis

Detailed characterization of precipitation is often necessary for performance optimization and computational materials design of metallic materials. With the improved TEM methodologies, quantitative analysis is now feasible thorough application of the methods described in this report. To exemplify this, we show some representative examples from recent literature with state-of-the-art results.

4.1. Performance optimization through advanced analysis of precipitate structure

The structure of precipitate and the precipitate–matrix interface directly determine the mechanism of precipitate–dislocation interactions and subsequently the magnitude of precipitation hardening. Cu is a widely used element to increase strength of various steels, e.g., maraging steels\cite{187–190} and ferritic steels\cite{191–193} by precipitation hardening, where a high number density of coherent body-centered cubic (bcc) Cu precipitates is sought for. Precipitates of Cu will first form as bcc Cu in the bcc Fe matrix due to the low mismatch and favorable nucleation conditions. However, after some aging time these bcc Cu precipitates will transform to semi-coherent 9 R Cu before they finally transform to the stable incoherent face-centered cubic (fcc) Cu structure. This process is thought to be size-related and the first systematic study of the crystal structure transformation in binary and ternary alloy systems dates back several decades and was carried out by Othen et al.\cite{194,195} using TEM. Recently, the crystal structure transition of Cu precipitates in multicomponent systems has been further unveiled taking advantage of the advancements in TEM instrumentation.\cite{95,196–202} Heo et al.\cite{196} used a Cs-corrected TEM and were able to identify untwinned 9 R Cu precipitates and twinned fcc Cu precipitate. Based on the results, they suggested that beam-orientation-dependent Moiré fringes could generate stray diffraction spots, which may have been misinterpreted as diffraction spots from 3 R structure of Cu precipitates, previously reported by Othen et al.\cite{194} These detailed analyses of the structure transition have facilitated better understanding of nucleation, growth and coarsening of the Cu precipitates, which is the premise for achieving a fine particle dispersion. The coarsening of Cu precipitates is of great practical interest for Cu precipitation-hardened steels applied in service under high temperature conditions.\cite{187} Since precipitate coarsening is one of the most crucial degradation processes for high temperature service of precipitation hardened steels,\cite{203} the key aspect for high temperature performance is to inhibit precipitate coarsening, where a lower precipitate coarsening rate means longer service life. One effective way to inhibit coarsening is to make use of a
core-shell structure of the precipitates.\textsuperscript{[204]} The shell that has a different composition and structure from the core can inhibit the diffusion of elements from the matrix to the core of the precipitates. With the capability of high-resolution structural and chemical analysis resulting from the aberration corrected microscopes, the nanoscale core-shell structure can be resolved nowadays. Figure 4 exemplifies the bcc Cu core-B2 Ni(Al, Mn) shell structure, where the B2 Ni(Al, Mn) shell acts as obstruction for the diffusion of Cu atoms and subsequently inhibits the growth and coarsening of the Cu core.\textsuperscript{[9]} There are plenty of similar examples as the ones presented above where the analysis of the precipitate structure has aided the current understanding and development of precipitation-hardened steels and other metallic materials.

### 4.2. Interface chemistry analysis for improved precipitation modeling

Most of the prevalent databases, theoretical models and setups for precipitation modeling need to be calibrated and validated by experimental data before predictive modeling is feasible.\textsuperscript{[106,205–208]} Thus, the application of advanced experimental measurements can facilitate the development and improve the accuracy of computational modeling.\textsuperscript{[209–211]} For instance, the quantitative characterization of local chemical composition information surrounding precipitates, that is, interstitial and substitutional elements at the matrix–precipitate interface, during the early stage of precipitation is crucial for shedding light on the nucleation and growth mechanisms, and for improving the modeling of precipitation kinetics in metallic materials. For a long time, the quantitative chemical analyses of precipitates within bulk materials and of their interfaces by analytical TEM have been limited using conventional thin-foil specimen due to complex factors influencing the analysis accuracy, e.g., the difficulty in distinguishing signals from embedded precipitates and the matrix, the differential etching rate of phases during specimen preparation,\textsuperscript{[212]} the effect of varying specimen thickness on beam spread,\textsuperscript{[213]} and the influence of interface misorientation with respect to the electron beam on concentration profiles.\textsuperscript{[214]} With the developments of advanced sample preparation methods and high resolution of EDS and EELS in advanced TEM, these issues can be combated and a reliable chemical composition analysis by high resolution EDS or/and EELS analysis on FIB lamellae with very thin and uniform thickness is now possible.\textsuperscript{[103,215,216]}

![Figure 4](image_url) TEM analysis of the bcc Cu core-B2 Ni(Al, Mn) shell nanoprecipitates in a Fe–2.5 Cu–1.5 Mn–4.0 Ni–1.0 Al (wt.%) alloy tempered at 500 °C for 5 h: (a) EELS elemental mapping acquired using a Gatan GIF Tridiem, (b) EDS elemental mapping acquired using a JEOL JED-2300T spectrometer, (c) [0 0 1]bcc HAADF and corresponding IFFT image by masking (0 1 0)\textsubscript{b2} reflection, captured under the camera length of 8 cm with a corresponding collecting angle of 100–267 mrad. All the measurements were performed using a JEOL JEM-2100F TEM equipped with double spherical aberration correctors for both probe-forming and image-forming lenses on thin-foil samples prepared by twin-jet electro-polishing (Adapted from Ref. [9]).
Figure 5a,b show TEM bright-field images and corresponding EDS mapping and line scans on cementite particles within a Fe–1Cr–1C alloy tempered for 5 s and 30 min at 500°C. The results show that the 5 s tempering sample has no obvious segregation of Cr atoms at the precipitate–matrix interface and the Cr/Fe atomic ratio within the precipitate is close to that of the alloy’s matrix phase. In contrast, the 30 min tempering sample shows Cr enrichment at the interface zone. The Cr/Fe atomic ratio around the precipitate–matrix interface in the 30 min tempering sample is far from the calculated equilibrium value of cementite, and the Cr/Fe atomic ratio at the center of the precipitate is equal to that in the matrix phase. These results indicate that only carbon diffusion occurs without long distance diffusion of substitutional elements (para-equilibrium) at the very early stage of cementite precipitation (5 s). With the progress of tempering (up to 30 min), substitutional elements start to diffuse but the composition of cementite precipitates is still far from ortho-equilibrium (full equilibrium) and also far from the spike composition in non-partitioning local equilibrium (NPLE). This study indicates that the formation of cementite during tempering of the Fe–Cr–C alloy does not follow the full local equilibrium composition at the interface. The actual composition of cementite is more close to para-equilibrium composition at the early stage of precipitation. Figure 5c demonstrates that ortho-equilibrium and para-equilibrium assumptions significantly influence the precipitation kinetics of cementite. This study on precipitate–matrix interface composition via analytical TEM on FIB lamella samples unveils the kinetics of cementite precipitation and suggests the necessity of improving precipitation modeling to enable predictive modeling of, for example, cementite precipitation kinetics and other cases of precipitation where it has been shown that the deviation from local equilibrium occur. It should be noted here that the analytical TEM in Ref. was performed with a conventional TEM on carefully prepared site-specific FIB samples. The resolution of the chemical analysis could be improved significantly by the application of an advanced analytical microscope.

4.3. Understanding of precipitation strengthening by in situ analysis of precipitate–dislocation interactions

Precipitation strengthening is influenced by many factors, including: size, structure, composition and chemical ordering of precipitates; interface coherency and orientation relationship of precipitate and matrix; number density, inter-particle spacing and particle size distribution. Based on whether a dislocation can pass through the precipitate or has to loop around a precipitate, the strengthening mechanism is usually divided into two types: shearing and Orowan looping. For impenetrable (incoherent, large coherent and high hardness/stiffness) precipitates, precipitation strengthening by the Orowan looping mechanism mostly depends on the size, volume fraction and inter-particle spacing. In contrast, for penetrable (small coherent and low hardness/stiffness) precipitates, precipitation strengthening by the shearing mechanism is the prevalent mechanism. It is more complex than the looping mechanism, including lattice misfit strengthening, modulus difference strengthening, ordered domain strengthening, chemical strengthening, etc. The precipitation strengthening by the shearing mechanism also depends on coherency, composition and chemical ordering in addition to the parameters relevant for the Orowan looping mechanism. As explained previously, all the quantitative parameters defining the precipitates can be characterized with state-of-the-art TEM techniques such as high-resolution imaging and spectroscopy, ACOM-TEM, 3D tomography, etc. The collection of all this information for improved modeling of precipitation strengthening is as important as the aforementioned optimization of precipitation kinetics modeling. The impact on modeling of precipitation strengthening that TEM techniques can exert is here exemplified by in situ TEM studies.

Ex situ TEM characterization cannot present a dynamic picture of the evolution of precipitate–dislocation interactions, and may easily cause misinterpretation of strengthening mechanisms. In contrast, in situ TEM in combination with advanced sample preparation and using a displacement controlled straining stage, has been successfully applied to monitor the dynamic interactions of dislocations with precipitates. At the early time, thin-foils prepared by the twin-jet electropolishing method was mostly employed under conventional TEM mode for in situ studies of relatively large precipitates, e.g., Al₃Sc and MgZn₂ precipitates (in the order of 100 nm) in Al–Zn–Mg–Cu–Zr alloys and Cr precipitates (in the order of 10 nm) in Cu–Cr–Zn alloys. With the introduction of FIB, micro-tensile specimens (in the order of 10 μm length and 100 nm thickness), with site-specific and orientation-specific characteristics, could be prepared. These specimens can thereafter be studied under STEM mode during in situ tensile loading. The STEM technique allows for simultaneous collection of a
wealth of information by BF, DF and HAADF detectors, as exemplified by the in situ STEM study of ϕ’ precipitates–dislocations interactions in Ni-based super-alloys in Ref. [231]. Recently, single crystalline nanopillars (in the order of 100 nm in all three dimensions) has been introduced into the in situ TEM study of precipitate–dislocation interaction. The single crystalline nanopillars successfully exclude the effect of boundaries on dislocation motion that exists in polycrystalline specimens prepared as either traditional thin-foils or micro-tensile specimen. In situ TEM investigations of compressive deformation of single crystal nanopillars has been used to study the deformation behavior of spinodally decomposed nanostructured Δ ferrite (with Fe-rich and Cr-domain sizes in the range of 5–10 nm) in 2205 duplex steels[232] and low-alloyed steel strengthened by interphase precipitates (in the range of 3–5 nm in diameter).[166] Those studies directly reveal the dynamic mechanical behavior and the influence of the nanoscale features on the developing dislocation structures. This is exemplified with Figure 6 from.[166] Through comparison of samples with different density of interphase precipitates, the effect of the interphase-precipitated nanoscale carbides on the deformation behavior was clarified and the Orowan looping mechanism for interactions between interphase precipitate and dislocations was suggested. Even though it is still challenging to directly capture the interactions of dislocations with these microstructural features in the order of several nanometers due to limitations like fast motion of dislocations, instability of nanopillars and the influence of strain contrast around dislocations, the recent improvements of in situ TEM analysis is facilitating improved understanding of deformation behaviors of nanoscale precipitates hardened materials. This work is, however, only in its infancy and it is expected to contribute significantly to guide

Figure 5. STEM-BF imaging of cementite on thin-foil samples with EDS mapping and EDS line scanning analyses of cementite in a martensitic Fe–1Cr–1C alloy tempered at 500 °C for (a) 5 s and (b) 30 min. The lamella specimens were prepared using a FEI Nova Nanolab 600 dual-beam system and measured using a FEI Titan Themis TEM equipped with spherical corrector for probe-forming operating at 200 keV (Adapted from Ref. [103]). (c) A comparison of volume fraction evolving with aging time under assumptions of ortho-equilibrium (full equilibrium) and para-equilibrium compositions.
improvements in the modeling of precipitation strengthening going forward.

5. Future prospects
5.1. Characterization of nucleation and early growth of precipitates

Analytical techniques such as STEM-EDS and STEM-EELS, particularly in aberration-corrected instruments, are effective for the qualitative composition analysis of precipitates with size of a few nanometers in bulk materials (as shown in Figure 4), but quantitative chemical analysis of these fine precipitates embedded in a solid matrix is challenging due to the signal from precipitates influenced by the signal from the surrounding matrix (as indicated by Figure 5). Extraction replica and electrolytic extraction are effective methodologies to extract precipitates out of the matrix, but these methods are usually much more challenging for

Figure 6. In situ TEM compression testing of a nanopillar (132 nm in width and 378 nm in length) with nanoscale interphase (Ti, Mo)C precipitates in a Fe–0.18C–1.45Si–1.47Mn–0.10Ti–0.19Mo (wt%) alloy tempered at 650 °C for 30 min: (a) engineering stress–strain curve with (b–i) individual frames. The nanopillar was prepared with instruments of Tecnai Nova 450 SEM, JEOL JEM-4000 FIB and JEOL JEM-9320 FIB using Ga⁺ ions. The in situ compression test was performed in a JEOL JEM-2010F TEM equipped with a Hysitron Piccolindenter (P95) at a nominal displacement rate of 0.5 nm s⁻¹ (From Ref. [166]).
extracting very fine particles with sizes of only a few nanometers in diameter.\cite{223} It should be mentioned here that even though APT holds capability of chemical analysis with atomic resolution, quantitative chemical analysis of precipitates/clusters with diameter below 2 nm is still a great challenge in APT due to trajectory aberrations, etc., though the precipitates can be readily detected.\cite{22} It is also difficult to know whether such precipitates are structurally distinct from the matrix by APT analysis.

The current understanding of composition and structure of a nuclei are mostly based on theoretical assumptions. For instance, in classical nucleation theory (CNT), the precipitate, starting from an embryo, is theoretically assumed to hold the identical composition and crystal structure with the final product and the nucleation event occurs when the embryo grows to a critical size.\cite{234} Due to its analytical simplicity, the CNT has been widely used in condensation of a vapor into a liquid, solidification of a liquid into a solid and solid–solid phase transformation for approximately one century.\cite{224} However, recent studies suggest that both the composition and crystal structure at the early stage of precipitation can be different with those of the final product. A two-step nucleation mechanism was proposed in solid–solid phase transformation and it was suggested that an intermediate liquid-like phase may exist in the nucleation process.\cite{235} By combining TEM and APT for studying G phase precipitation, a similar two-step nucleation mechanism was proposed, where the first step is the spontaneous growth of solute clusters to a critical size, before the second step where a structural change of the solute clusters of a critical size occur to form a compound controlled by a solute enrichment process.\cite{236} This structural change of the precipitates from clusters may change the obstacle strength against dislocation gliding, and may trigger embrittlement and influence the lifetime of the material product.

Even today, experimental techniques that can accurately analyze the composition and structure of precipitates during nucleation and early growth are very rare,\cite{237} but TEM is without doubt one of the most promising techniques to tackle these challenges. Specifically, for precipitates of interest holding different crystal structures compared to the matrix, electron diffraction by TEM is a capable technique to capture nucleation features, as exemplified in Refs. [9,236]; the cluster microstructure of short-range order domains on the scale of Ångstrom can be directly imaged using energy-filtered dark-field imaging in TEM\cite{238}; The precipitation pathway of (Ti, Mo)C that embryo cluster grows into NaCl type nanosized structure through GP cluster has been revealed combining FIB site-specific lift-out sample preparation and HR-STEM operating at 300 kV with double aberration correctors.\cite{239} In addition, the mechanism of nucleation can be revealed through innovative design of experiments under TEM, e.g., the four dimensional (including time) atomic structure of early stage nucleation of synthesized FePt nanoparticles were observed using the TEAM (Transmission Electron Aberration-

| Methods                  | Advantages                                                                 | Disadvantages                                                                 |
|--------------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Twin-jet electro-polishing | i. Time and cost efficiency  
ii. Large thin area               | i. Differential thinning for multiphase materials  
ii. Not site-specific  
iii. Inaccurate control of thickness  
iv. Sample volume is too large for magnetic materials which causes electron beam distortion |
| Focused ion beam          | i. Site-specific  
ii. Accurate control of thickness  
iii. Preferred for magnetic materials, no electron beam distortion due to small volume lamella | i. Ion beam damage  
ii. Long preparation time and high cost |
| Chemical extraction       | i. Elimination of the influences from matrix for chemical and structural analyses of precipitates  
ii. Elimination of magnetic influences of matrix on electron beam  
iii. More penetrable by electron beam  
iv. Better contrast between precipitates and background | i. Lack of interface and matrix-precipitate information  
ii. Challenging for very fine precipitates  
iii. Possible chemical modifications of precipitates  
iv. Challenging to extract representative particles in case of bimodal distribution |
| Electrolytic extraction   | i. Same with chemical extraction  
But, is less likely for fine precipitates to be dissolved  
iii. Can dissolve large volume of materials, which is beneficial for volume fraction analysis and identification of multiple precipitate phases simultaneously  
| i. Lack of interface and matrix-precipitate information  
ii. Selections of electrolyte and electrochemical potential for specific types of materials and precipitates could be challenging. |
corrected Microscope) 0.5, the so-called world’s best microscope, and a generalized Fourier iterative reconstruction algorithm (GENFIRE).\cite{36} To conclude this section, further improvements in TEM techniques and possibly correlated APT could aid to provide novel data on the nucleation and early growth stages during precipitation. That could have large implications on our understanding of precipitation and theories for nucleation and growth.

5.2. *In situ* characterization of precipitates

Precipitation crystallography is crucial for understanding orientation, morphology, habit plane, etc., of precipitates in crystalline matrices.\cite{240–243} However, in comparison to the well-developed thermodynamic\cite{244} and kinetic\cite{245} theories of precipitation, the knowledge of precipitation crystallography is rather rudimentary.\cite{246} A complete understanding of precipitation thermodynamics, kinetics and crystallography is necessary to reveal the full picture of precipitation reactions in metallic materials, before controlling precipitation hardening.\cite{247} For example, Matsukawa et al. recently\cite{248,249} demonstrated that by tuning the orientation of soft precipitates to make their slip plane non-parallel to that of the matrix, the magnitude of precipitation hardening is increased due to the crystallographic mismatch making the soft precipitates unable to cut through by gliding dislocations. In this case, the soft metallic precipitates work as effectively as hard nonmetallic compounds\cite{250} for precipitation hardening. Likewise, hard precipitates are also shearable if their slip plane is aligned parallel to that of the matrix.\cite{251} With its incomparable status among various characterization instruments for crystallography analysis, TEM is opening up a variety of opportunities for monitoring precipitation crystallography information in real-time and real environments. For example, Du et al. verified for the first time,\cite{158,252} with real-time *in situ* TEM observation of dislocation emission at elevated temperature, that dislocation activity assists the growth of austenite precipitates and obtained quantitative data to explain the strain and stress field associated with interface migration. Not only precipitate growth, precipitate splitting, precipitate structure transformations, etc., as mentioned in Subsection 3.3, but also the precipitate–dislocation interactions as exemplified in Subsection 4.3, are appealing for further applications of *in situ* TEM techniques.

5.3. High-throughput analysis of precipitates

EBSD in SEM has become a routine technique for automated acquisition of orientation and phase data in inorganic materials, but it has been rarely used for the characterization of nanoscale precipitation due to its resolution limit of a few tens of nanometers depending on SEM resolution and investigated materials. In contrast, SEM-based TKD\cite{253–257} which uses the same setup with EBSD except that thin-foil TEM specimens in transmission mode is used, can achieve a resolution limit of about 5–10 nm due to the reduced interaction volume between the electron beam and the thin-foil sample. TKD has been used in studies of nanoscale precipitates, e.g., $M_23C_6$ with size around 30 nm in steels,\cite{255} Al-Cu precipitates with size around 50 nm in Al-Li alloys\cite{256} and cementite particles in steels.\cite{257} However, the resolution of SEM-based TKD is still far from satisfactory for the analysis of nanoscale precipitates, where the size is usually below 20 nm. Overcoming the limited resolution of the EBSD and TKD techniques in SEMs, ACOM-TEM, as a novel EBSD-equivalent technique for TEM, gives much higher spatial resolution, and thus, provides opportunities for analysis of nanoscale precipitates.\cite{154} ACOM-TEM shows strengths beyond EBSD not only in resolution, but also in its lower sensitivity of the applied spot diffraction to deformation and crystallite size,\cite{156} compared to Kikuchi diffraction used in EBSD and TKD. Examples of applications that would tremendously benefit from this technique is the analysis of multiple precipitation, such as, in CrMoV-alloyed carbon steels,\cite{106,258–261} where multiple carbides, including MC, $M_2C$, $M_3C$, $M_6C$, $M_2C_3$ and $M_{23}C_6$, can precipitate and transform depending on the thermal conditions and contents of alloying elements. ACOM-TEM,\cite{155} together with carbon extraction replica to avoid the influence of matrix on spot diffraction pattern recognition of precipitates,\cite{154} would be efficient to determine the type, size, morphology, etc. of multiple precipitation in various metallic materials. With the development of postprocessing algorithms as demonstrated by Rauch and Vérón,\cite{262} the orientation map of embedded nanoprecipitates in a crystalline matrix, i.e., when thin-foil specimen is employed, can also be obtained.

6. Summary

TEM, a versatile technique for precipitation characterization, has historically been facilitating the understanding of precipitation and precipitation hardening, and over the past decades TEM has also stimulated
the optimization of performance of metallic materials through precipitation engineering. The recent advancements in TEM-based techniques, sample preparation methodologies and algorithms for data analysis have significantly strengthened the capability of the premier TEMs. Incorporated with recently developed aberration-corrected techniques, TEM provides an irreplaceable and indispensable instrumentation for precipitation-related research in metallic materials, combining morphological (imaging), chemical (spectroscopy), structural (diffraction), three-dimensional (tomography), environmental (in situ) analyses down to the Ångström scale.

Even at present with the strong emphasis on computational materials science, TEM plays a key role in guiding the creation of databases, the development of theoretical models and the setup of modeling, calibrating and validating the precipitation kinetics modeling and property modeling. Moreover, together with well-developed theories of precipitation thermodynamics and kinetics, the progressing understanding of precipitation crystallography, facilitated by the development of TEM techniques, is unveiling the mechanisms of precipitation reactions in a quantitative way.

TEM development is still ongoing to become even better for precipitation studies by integrating advancements in instrumentation, sample preparation methodologies and high-end analytical techniques/computational methods. Further developments of TEM-based methodologies are promising for continuously expanding the current knowledge of precipitation toward a complete understanding of nucleation, precipitate–matrix interface and precipitate–dislocation interaction, and toward a more automated and intelligent way of analysis.

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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.

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