Contiguous hetero-structures and co-existing morphological derivatives of preferentially grown carbo-nitrides in long-term aged SS 316LN with varying nitrogen concentration

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ABSTRACT

SS 316LN with varying nitrogen content is subjected to thermal aging for 20,000 h at 650 °C to assess long-term structural integrity under operational conditions in nuclear reactors. While the annealing twins and heterogeneous grain evolution by bimodal division are independent of chemical composition, the type, size, and morphology of evolving secondary phases are characteristic of nitrogen concentration. Color contrast in bright field optical microscopy combined with transmission electron microscopy reveals the presence of three major precipitate phases; M₂₃(C, N)₆, Fe₂Mo intermetallics, and Cr₂N. Contiguously formed hetero-structures of Fe₂Mo/Cr₂N are quantified, and extensive formation has been observed in steels with high nitrogen content (0.14 wt. % and 0.22 wt. %). In addition to the grain boundary carbo-nitrides, the morphological derivatives of intra-granular M₂₃(C, N)₆ precipitates with cube-on-cube orientation relationship such as (1) isolated cubes, (2) primary stringers/strings of cubes, (3) secondary stringers/clusters of branched primary strings, and (4) clusters of laths are identified. The stringers and laths are preferentially grown in {111}/ < 110 > γ. The growth plane and crystallographic variants of primary and secondary stringers are exclusively identified from optical micrographs. All varieties of M₂₃(C, N)₆ are prominent in the sample with 0.22 wt. % nitrogen whereas, clustering of stringers and laths are absent in steels with lower nitrogen concentration. Overall mechanical properties reform by the precipitation strengthening effect due to the excess nitrogen content.

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Introduction

The developing strategies of high nitrogen steels focus on mechanical properties such as strength, toughness, creep resistance, and stress corrosion resistance of engineering components hence ensuring their extended and economic utility [1]. With better solid solubility than carbon, nitrogen—a strong austenite stabilizer acts as an interstitial solid-solution strengthener. The yield strength of nitrogen added steel exceeds standard carbon-based steel, which can improve by cold working [2, 3]. Currently, in fast breeder nuclear reactors, SS 316LN with optimized nitrogen composition is the structural material for primary side components [4]. Nitrogen addition can enhance the resistance to high-temperature fatigue and creep failure of the components experiencing cyclic thermal stresses, steady-state loading, and thermal transients in addition to the mechanical load variations during normal reactor operations [5–8].

It is well established that for SS 316LN, the microstructures like grain size morphology and twin density are least affected by heat treatment/prolonged annealing [9]. However, long-term thermal aging promotes the formation of thermally activated secondary phases containing both interstitial strengtheners, which causes a reduction in the high-temperature stability of the alloy [2, 10]. The major
precipitate phases expected to form in the matrix are carbides, \( \sigma \), \( \eta \), and \( \text{Cr}_2\text{N} \) [11–14]. The chemistry and distribution of \( \text{M}_{23}\text{C}_6 \) carbides in SS 316LN aged for 300 h have been documented previously, and chromium depleted regions are quantitatively measured [15]. Depletion of chromium near the grain boundaries resulting from the grain boundary precipitates happens even in ultra-low carbon SS 316LN subjected to long-term heat treatment in the sensitization temperature range. Larger-sized grain boundary precipitates with nitrogen content [9] indicate their contribution as a precipitate strengthenener than an interstitial strengthenener.

In the previous work of the present authors [16], the mechanical properties of SS 316LN with varying nitrogen content have been analyzed and correlated with microstructural evolution. The identified precipitate phases are \( \text{M}_{23}\text{C}_6 \) carbides, \( \text{Fe–Cr–Mo intermetallics} \), and \( \text{Cr}_2\text{N} \). The results show a rise in precipitate density with the nitrogen content. The overall microstructural effect by precipitate strengthening mechanism links to the tensile behavior. For advancing the present study, a thorough investigation requires because the microstructure and precipitation kinetics in long-term aged samples can be vibrantly diverse. Mutual interaction of structural heterogeneities, morphological derivatives of secondary phases, and crystallographic variant selection are some of the expected phenomena. Hence, present study aims a comprehensive microstructural analysis and the precipitate interaction with defect structures in SS 316LN with varying nitrogen content.

Traditional methods to identify evolving precipitates and their characteristics involve various techniques such as carbon replica of precipitates for transmission electron microscopy (TEM), extracted residues for X-ray diffraction, and electron backscattered diffraction (EBSD) analysis for fine features with improved spatial resolution using field emission gun. The instrument operating skills (for sample preparation and acquiring images) and the expertise in data analysis are the essential requirement for the above techniques. In TEM-based methods, the probed area is minimal. In the present study, bright field optical imaging under reflection mode has been exclusively used for differentiating the precipitate phase by color contrast. Moreover, TEM analysis is used as a supportive measure for comparing the optical microscopy results and for chemical analysis. The authors have adopted an optimal sample-preparation method only with the vibratory polishing technique, which made the sample preparation simple as it does not involve further etching steps for morphological and structural identification of precipitates. Optical microscopy has opted as a potential tool to efficiently and accurately process a huge amount of data, hence overall microstructure features from large regions can be visualized, and the quantification of characteristic features might be comprehensive.

Materials and methods

Alloy preparation

By implementing a double melting process, four commercial-scale heats of SS 316LN with 0.07, 0.11, 0.14, and 0.22 wt.% N (hereafter designated as N07, N11, N14, and N22, respectively) were produced. An air induction melting furnace with a 2.5-ton capacity was used for the primary melting of each heat. The precision in chemical compositions was closely controlled by using pure raw elements. Necessary steps were followed for other minor elements to have close control in composition. Required nitrogen concentration was achieved by using nitride ferrochrome. The electro-slag refining process was adapted as the secondary melting process to ensure limited inclusion content in the steel. The ingots from the electro-slag refining process were thermo-mechanically deformed into slabs followed by plates of 22-mm-thickness by implementing hot forging and hot rolling subsequently. The final solution annealing treatment was carried out at about \( \sim 1100^\circ \text{C} \) followed by water quenching.

The chemical composition of as-received samples of four heats is given in Table 1. Rectangular blanks of dimensions, 160 \( \times \) 22 \( \times \) 20 mm, were cut and further solution annealed at 1090\( \circ \text{C} \) for 1 h followed by water quenching. Long-term aging experiments in each sample were conducted at 650\( \circ \text{C} \) for 20,000 h.

Characterization

The samples for optical microscopy were prepared by the conventional route of mechanical grinding and polishing. Fine grinding with SiC (Silicon Carbide) papers was carried out up to the level of 2400 grid paper. Final polishing was carried out using a vibratory polisher (QATM Saphir Vibro Vibratory
Polishing Device). In vibratory polisher, two different polishing agents; colloidal silica and alumina suspension had been used separately in each sample for revealing various microstructure features. Polishing at optimizing conditions of vibration frequency was continued for 24 h to assure good contrast in optical imaging. In contrast to the conventional route for optical microscopy, there was no further etching process conducted. Optical microscopy by bright field color contrast imaging in reflection mode had been carried out in Zeiss optical microscope.

Electron transparent thin samples for characterization using analytical transmission electron microscopy were prepared by twin jet polishing using perchloric acid:methanol (in 1:9 ratio) electrolyte. Diffraction contrast images and selected area diffraction patterns were recorded by transmission electron microscopy in Philips CM200 ATEM operated at 200 kV equipped with Energy Dispersive X-ray Spectroscopy (EDS) detector. HAADF-STEM (Scanning transmission electron microscopy by high angle annular dark field) imaging and EDS elemental mapping were carried out in Talos (Thermofisher Scientific) at an accelerating voltage of 200 kV. JEMS electron microscopy simulation software version 4.46 [17] was used for the analysis and simulation of diffraction patterns. Additionally, stereographic projections and Wulff net analysis are carried out for identifying the growth directions and variant selections of precipitates.

**Results**

Microstructural analyses of N07, N11, N14, and N22 steels have been carried out to study the morphological characteristics using optical microscopy and the chemistry and crystallography of precipitates using transmission electron microscopy.

| Sample | Cr      | Ni  | Mo   | Mn | C     | P     | S     | N     | Fe  |
|--------|---------|-----|------|----|-------|-------|-------|-------|-----|
| N07    | 17.5    | 12.2| 2.49 | 1.70| 0.03  | 0.013 | 0.0055| 0.07  | Bal |
| N11    | 17.5    | 12.2| 2.5  | 1.72| 0.03  | 0.013 | 0.0055| 0.11  | Bal |
| N14    | 17.5    | 12.1| 2.53 | 1.74| 0.03  | 0.017 | 0.0041| 0.14  | Bal |
| N22    | 17.5    | 12.3| 2.54 | 1.70| 0.03  | 0.018 | 0.0055| 0.22  | Bal |

Microstructural characterization of grains and precipitates using light optical microscopy

Figure 1(a-d) shows optical images from samples prepared by vibratory polishing with alumina suspension. The bright-field optical contrast shows the presence of annealing twins. In long-term aged SS 316 LN, the most feasible annealing twins lie on \{111\} planes. The contrast depicts the V-shaped double twins randomly distributed in several grains, which can be represented by the sides of the well-known Thompson tetrahedron [18, 19]. The geometric relationships of four equivalent \{111\} slip planes in fcc lattice are illustrated by the Thompson tetrahedron. The angle between any two slip planes is 70.53° (or 109.5°) and which is visible in some grains lying on exact projection with the optic axis. Qualitative analysis on these micrographs reveals the resemblance in twin morphology thereby implying that nitrogen concentration has a negligible role on twin density.

Optical microscopy reveals the grain microstructure (Fig. 1(e–h)) in samples prepared by the second method where colloidal silica has been used as the final polishing agent in the vibratory polisher. Bright field contrast in optical imaging projects a ditch microstructure for the grains indicates the sequential formation of grain boundary precipitates which will be discussed in subsequent sections. Equi-axed grains of size ranging from 10 μm to 410 μm are visible in all samples with a slight bimodal division in morphology. By analyzing nearly 1000 grains from the N22 sample, the graph of grains size vs frequency counts (Fig. 2a) has been drawn which shows the maximum counts at ~ 50 μm and ~ 350 μm for smaller and larger grains, respectively. Figure 2b depicts the grain size vs. area average grain size where the heterogeneous grains with bimodal nature are demonstrated by Gaussian fit. The similarity of grain size distribution in each sample is obvious from the images. This analysis illustrates that there is no
significant variation in grain size and its distribution with the nitrogen concentration.

Figures 3a and b present a representative microstructure with much finer details of precipitate contrast at reflection mode in optical imaging. Figure 3b highlights the typical bright-field color contrast (rectangle box) for various features/precipitates. The image depicts the presence of a substantial amount of intra-granular and inter-granular precipitate formation with two major color variations; amaranth and green. Lean grain boundaries are decorated by cascades of elongated amaranth precipitates (thickness \( \sim 0.5 \mu m \), length \( \sim 1 - 2 \mu m \)) tangential to the boundary, whereas irregular bigger precipitates (size \( \sim 1 - 2 \mu m \)) are common in densely populated grain boundaries. The green features form adjacent to the amaranth ones in both thin and dense boundaries. The non-uniform distribution of inter-
granular precipitates can be attributed to the degree of strain at the grain boundaries. It is also observed that the twin boundaries are partially covered with precipitates, mostly amaranth ones. The intra-granular precipitates of both amaranth and green type are randomly distributed all over the grain. However, there is a considerable variation in the number density, size, and morphology of the precipitates while considering the images from each sample with varying nitrogen content. For example, some amaranth precipitates selectively elongate up to 5 μm (indicated with a white arrow in Fig. 3b) in some samples, meanwhile, the green ones elongate arbitrarily. Moreover, an increase in total secondary phase formation with nitrogen concentration is observed. Before commenting on each colored feature, the chemistry and crystallography are characterized by using transmission electron microscopy as follows.

**Identifying the crystallography of precipitates**

The TEM micrographs in Fig. 4 demonstrate the evolution of precipitate microstructure in SS 316LN during long-term aging. The bright-field image (Fig. 4a) from sample N07 depicts the distribution of inter-granular and intra-granular precipitate phases. Precipitate phases have faceted cuboidal, elongated, and irregular morphologies with a size range from 100 nm to 1 μm. The SAD (selected area diffraction) pattern recorded from grain interior in Fig. 4b shows fcc γ matrix along <-110> γ zone axis, where reflections from cuboidal shaped precipitates are also present. Overlapping of the third-order precipitate reflection with the first-order matrix reflection implies the cube-on-cube orientation relationship and coherency between matrix and precipitate, which is well established for M23C6 type precipitate [20, 21]. These correlations are confirmed by simulating the diffraction patterns of γ matrix (a = 3.56 Å, Fm-3 m) and M23C6 precipitate (a = 10.67 Å, Fm-3 m) using JEMS (Java-based Electron Microscopy Software) [17] and by generating the combined diffraction pattern as shown in Fig. 4c. Chemical analysis using TEM-EDS indicates the presence of Cr, Fe, and Mo in this carbide in descending order of composition. The point EDS experiment also reveals the presence of nitrogen along with carbon, thus the precipitate can be more specific as M23(C, N)6 carbo-nitrides.

The Cr-enriched M23(C, N)6 precipitates are also populated in grain boundaries but differ in size and shape (marked on Fig. 4a). They are comparatively larger in size with irregular morphology. Diffraction analysis on these grain boundary carbides reveals that they have a coherent interface and cube-on-cube orientation relationship with one of the matrix grains from which it has been grown [20, 21]. On the coherent matrix side, the precipitate has a faceted morphology while shape irregularities are mostly visible on the other side. Figure 4d shows the M23(C, N)6 precipitates occupied in the twin boundary and near regions. By characterizing the selected area diffraction pattern taken from the twin boundary (Fig. 4e), the zone axis has been identified as [011]γ, and the twin plane is (111)γ, which is a coherent twin boundary [20]. The traces of coherent precipitates in both sides of the twin plane with a cube-on-cube orientation relationship are visible in diffraction patterns as satellite reflections [21]. The dark field

**Figure 3** Optical images taken from N11 depict various precipitates by color contrast (vibratory polishing with colloidal silica).
image is taken from the selected reflections (which include the reflections from precipitates embedded in both sides of the twin) marked inside the circle in the SADP. A faint contrast of one of the carbides on the twin boundary grown toward one side of the twin is also visible in the image (marked with an arrow). It is observed that, in the twin boundary, the coherent precipitates like M$_{23}$(C, N)$_6$ always grow towards either side of the twin but not across the boundary.

Figure 5(a–d) shows the bright field image, selected area diffraction pattern, and dark field image recorded from the second kind of precipitate found in all steels having irregular or arbitrarily elongated shapes. The chemical analysis using EDS shows that the precipitate is rich in elements such as Fe and Mo. The diffraction pattern analysis (Fig. 5a and d) shows the structural dimensions of this phase match with η-Fe$_2$Mo Laves Phase having hexagonal symmetry. The diffuse streaks along the preferred direction in the diffraction pattern and lamellar morphology in bright-field and dark-field images indicate the presence of planar defects/stacking faults in the intermetallic phase. These elongated precipitates with crammed planar defects are also found nearby the grain boundaries (Marked as Fe$_2$Mo in Fig. 4a).

Furthermore, in high nitrogen steels (N14 and N22), Fe$_2$Mo intermetallic is mostly contiguous with yet another precipitate phase as seen in Fig. 5(e–h). Diffraction analyses with simulation experiments confirm that these are Cr$_2$N precipitates having hexagonal symmetry with Pearson’s symbol hP11. The diffraction contrast images demonstrate the coexistence of Cr$_2$N with Fe$_2$Mo intermetallic phase. Laves phase crystals likely act as heterogeneous nucleation sites for Cr$_2$N precipitate or vice versa. Scanning transmission electron microscopy by high angle annular dark-field imaging (STEM-HAADF) combined with EDS mapping (Fig. 6) gives an unambiguous depiction of chemical composition in each phase. Substantial nickel enhancement is observed in intermetallic; however other substitutional elements are completely absent. Moreover,
manganese and carbon are preferentially segregated within Cr$_2$N precipitates, by replacing chromium and nitrogen atoms correspondingly.

From selected area diffraction pattern analysis of varieties of precipitates, and comparison with optical micrographs following conclusions can be made: the grain boundary precipitates are carbo-nitrides particularly M$_{23}$(C, N)$_6$ precipitates (‘amaranth’ feature in optical micrograph) and Fe$_2$Mo intermetallic (‘green’ feature in optical micrograph) form adjacent to that. The twin boundaries are decorated mostly with M$_{23}$(C, N)$_6$ precipitates with faceted cuboidal morphology. Inside the grain, a substantial amount of cuboidal M$_{23}$(C, N)$_6$ precipitates and elongated/
irregular Fe$_2$Mo intermetallics are randomly distributed. In high nitrogen steels, N14 and N22, Cr$_2$N forms frequently with Fe$_2$Mo intermetallic by sharing the interface in a contiguous manner. The picturization of contiguous Fe$_2$Mo/Cr$_2$N precipitates is seen in Fig. 7, where the typical red feature (Cr$_2$N) is frequently associated with green ones. Figure 7 demonstrates how resourceful the optical microscopy (of vibratory polished samples under optimal conditions without any etching process followed) is to reveal the presence of two or more crystallites of both kinds (Fe$_2$Mo and Cr$_2$N) sandwiched each other.

** Preferentially grown M$_{23}$(C, N)$_6$ stringer**

Optical micrographs provide an expansive view of precipitate distribution and geometry easily and precisely, thus, an interesting phenomenon of stringer morphology for M$_{23}$(C, N)$_6$ precipitates (marked in Fig. 3b and 8) is observed inside the grains. Micrographs prove these stringers form prominently in N07, N11, and N22 steels. In N14 steel the stringers are hardly seen, whereas, in N22 steel, they are heavily populated (Fig. 8c). The stringer morphology of M$_{23}$(C, N)$_6$ precipitates in the same sample is reported using SEM/EBSD phase map in our previous work. The maximum length of the stringer can be measured as 5 μm, provided, the long axis of the stringer is parallel to the planar view of the image (stringers in Fig. 8c from N22 steel appear shorter might be due to the off-axis view). The measured width is nearly 500 nm. Observations demonstrate that the growth direction of stringers is preferential consequently, there might be multiple crystallographic variants existing within a single grain. Two variant selections are visible and separately marked with black and white arrows in Fig. 8a. Thorough

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**Figure 7** Color contrast in optical micrographs shows the contiguous precipitation of Cr$_2$N with Fe$_2$Mo as joined red and green features in a 316LN 14 and b 316LN 22.

**Figure 8** Primary strings of M$_{23}$(C, N)$_6$: Optical micrographs of preferentially grown M$_{23}$(C, N)$_6$ stringers having color contrast of amaranth (lamellar) appear in a N07 (two crystallographic variants are marked with white and black arrows), b N11, and c N22 samples.
investigation in optical images reveals, generally, the stringers are parallel to the twin as seen in Fig. 8b, which will provide a hint to identify the directional preferences of the precipitate growth. While relating with the well-known fact, the annealing twins usually form on close-packed \{111\}/\text{\lt}112\text{\gt} plane/direction and are coherent for fcc structure \cite{20, 22–24}, it can be confirmed that the stringers of M\textsubscript{23}(C, N)	extsubscript{6} grow on \{111\} planes of austenite matrix.

**Clustering of preferentially grown M\textsubscript{23}(C, N)	extsubscript{6} stringers**

Figure 9 shows a typical sequential formation of M\textsubscript{23}(C, N)	extsubscript{6} precipitates (circled), where the preferentially grown branches/stringers share a common baseline identified in N22 steel. Each branch of \(~ 10 \mu\text{m}\) length is arranged in a common habit plane within \(~ 1 \mu\text{m}\) interval. Generally, these clusters are grown up to hundreds of micrometers. Typical features of these clusters or secondary stringers are: (1) the baseline may shift or bend by its trajectory, however, the branches keep parallelism consistently, (2) there are regions where the baseline plane is perpendicular to the growth direction of branches (marked in Fig. 9a), (3) preferentially grown M\textsubscript{23}(C, N)	extsubscript{6} stringers (primary stringers in Fig. 8) are comparatively less in the vicinity of the clusters of stringers, and (4) the ends of the baseline of each cluster can be grain boundaries or twin boundaries or mixed.

Directional preferences and variant selections of secondary stringers are also identified by analyzing optical micrographs and by relating to the twin planes. In Fig. 10, three secondary stringers are evident (marked as A, B, and C), where ‘A’ and ‘B’ are from the same grain, whereas ‘C’ forms nearby grain. Cluster ‘A’ starts and ends in twin boundaries, whereas, ‘B’ and ‘C’ originate in grain boundary but the other end’s contrast diminishes in the matrix. Even though there is poor contrast at the end of its baseline, a detailed analysis throughout the sample clues the role of twin boundary in terminating the cluster formation. In cluster ‘A’, the branches/stringers are formed on the planes parallel to twins on \{111\}γ planes, indicating \{111\} plane is the growth direction.

**Figure 9** Secondary stringers of M\textsubscript{23}(C, N)	extsubscript{6}: Optical micrographs from N22 samples prepared in vibratory polisher with silica colloidal solution show clusters: a Branching of amaranth precipitates/M\textsubscript{23}(C, N)	extsubscript{6} on a common baseline in a preferential direction, b The highlighted image shows a better contrast for the textured precipitate as clusters of stringers/branches in a common baseline.

**Figure 10** Secondary stringers of M\textsubscript{23}(C, N)	extsubscript{6}: Two variants of clusters of preferentially grown M\textsubscript{23}(C, N)	extsubscript{6} stringers are identified in single grain indicated as ‘A’ and ‘B’, where A starts and ends at twin boundaries (TB).
plane. In the same grain, the branches of the second cluster ‘B’ grow along 109° angle from the plane of branches in ‘A’. The angle between two opposite body diagonal (along \(<111>\)) is 109.5°, and which can be measured exactly in the zone axis of \(<110>\) \(\gamma\) implies the grain with ‘A’ and ‘B’ clusters lie exactly at \(<110>\) \(\gamma\) zone axis. Hence, the image contains grain in \(<110>\) \(\gamma\) projection depicts two variants of secondary stringers of M\(_{23}(C, N)_6\) grow in two different (111) planes.

Discussion

Color contrast for precipitate phases without etching

Conventional methods of chemical etching are practiced for revealing the twin boundaries [9] and other planar defects in materials. However, in the present study, vibratory polishing at optimized conditions with colloidal silica and alumina suspensions for 24 h is implemented for revealing the microstructural features without any further etching process. The twins are emerged by bright-field reflection mode in optical microscopy by using alumina suspension as the final polishing agent. Optical lithography takes place by mechanical action with nanometer-sized abrasive particles of alumina which enables visualization of twin microstructure. Hence, the present study establishes prolonged polishing in vibratory polisher with alumina suspension reveals the presence of planar defects.

Considering the volumetric defects, there are numerous studies to distinguish different precipitate phases in optical micrographs by chemical etching or color tint etching [25, 26]. Precipitate phases are distinguished in optical micrographs with color contrast by using colloidal silica as the final polishing agent. Both mechanical and chemical action (CMP-Chemical mechanical polishing) from the solution additives in colloidal silica [27] instigate preferential material removal, hence the chemically un-homogenized precipitates reflects as individual optical entities. While illuminating the sample, each feature/region will alter the wave-front, and hence, the light absorption to give different optical disparities that emerge as unique contrast (identified with different grey-scale) [28]. These disparities are materialized from the light absorption and refractive index of the material, which is intrinsic for each feature. The contrast mechanism is similar to the shadow effect in etched samples, where the formation of reliefs and up/downs due to the hardness variation of precipitate phases can happen differently with different polishing agents. Polishing parameters of vibratory polisher have a crucial role to play in projecting the required features in microstructure, thus optimization for polishing cloth, solution, and time has been carried out for each sample.

In color contrast bright field imaging, the grayscale is converted to the opted wavelength (BGR-blue green red) provided by the instrument software. The color contrast assigned to each precipitate phase is the combined effect from the vibratory polishing techniques and optics of the image formation in bright-field optical imaging. Thus amaranth, green, red, and grey colors represent M\(_{23}(C, N)_6\), Fe\(_2\)Mo, Cr\(_2\)N, and matrix, respectively. In addition to the differentiation of precipitate phases, formation ways (contiguous Fe\(_2\)Mo/Cr\(_2\)N and morphological derivatives of M\(_{23}(C, N)_6\)), the plane and direction of precipitate formation, and variant selections for M\(_{23}(C, N)_6\) stringers/clusters are successfully imaged and analyzed exclusively by color contrast in bright field optical microscopy.

Bimodal nature in the grain size distribution of SS 316LN

All steel varieties with varying nitrogen content in the present study exhibit a similar trend of bimodal distribution with the coarse and fine grains. A moderate difference between the maxima of smaller grains (50 \(\mu m\)) and bigger grains (350 \(\mu m\)) is observed. However, the effect of grain distribution on overall mechanical properties and engineering performances will be significant because bimodal grain distribution is one of the microstructural strategies for implementing a good combination of strength and ductility to the system. Literature reports a bimodal division (20—250 \(\mu m\)) for SS 316LN with a nitrogen concentration of 0.174 wt. % [29], where it is shown that the range of grain size variation will be minimal for lower nitrogen concentration. The bimodal nature of grain distribution has been observed in the solution annealed 316LN as well. Images from existing literature show the proof [30, 31], however, the observation has not been specifically mentioned. Recently, studies on nitrogen added High Entropy
Alloys (HEA) illustrate the heterogeneous grain size distribution trending to have a bimodal division [32] which won’t compromise the strength-ductility trade-off. Bimodal division of single order of magnitude of SS 316LN may contribute to the superior creep resistance property along with other upgraded mechanical properties. However, the current study doesn’t observe any significant variation of the bimodal trend with nitrogen content for a limited range of nitrogen concentrations from 0.07 to 0.22 wt. %.

Contiguous hetero-structures of Fe₂Mo/Cr₂N in SS 316LN

The evolution of Cr₂N precipitates and intermetallic in high nitrogen steels is documented in the literature in many aspects. The likelihoods of formation of σ phase and χ phase under high-temperature aging treatment (between 850 °C and 900 °C) are established theoretically and experimentally [33]. The Cr₂N precipitation in 17% Cr, 13% Ni, 5% Mo low carbon steel with 0.25 wt% nitrogen was first reported in 1969 where Fe₂Mo precipitation also has been identified [34]. The formation of Fe₂Mo intermetallic on the Cr₂N/Matrix interface has been reported in 9Cr-1Mo steels by analyzing carbon replica samples in transmission electron microscopy [35–37]. Co-precipitation of Fe₂Mo and Cr₂N by the contiguous way has been identified by amplitude contrast imaging in high alloyed austenitic stainless steel containing 0.54 wt.% of nitrogen [38]. The streaks observed in the SADP have been explained as the planar fault in the intermetallic. In contradictory, the joint formation of the Cr₂N/σ phase has been reported in steels containing the elemental composition of 17.94 Cr; 18.60 Mn; 2.09 Mo; 0.89 N; 0.04 C; balance Fe in wt. % [39]. It is reported that alloys with high manganese content are prone to have the side-by-side formation of the Cr₂N/σ phase [40–42].

In the present study, the analysis of contiguous Fe₂Mo/Cr₂N (green/ red) precipitates has been carried out, and the area density and frequency of occurrence are quantified from the optical micrographs. By imaging a large area, the average distance between two precipitate combinations is roughly calculated as 80 µm and 50 µm for N07 and N11s-steels, respectively. In N14 steel, the occurrence of contiguous precipitates repeats at 3–10 µm, whereas, in N22, the frequency is quite high; the co-existing Fe₂Mo/Cr₂N of 1–2 µm size appears within 2 to 5 µm distance. The area density of Fe₂Mo/Cr₂N precipitates is measured as 0.0001%, 0.005%, 0.34%, and 2.7% for N07, N11, N14, and N22, respectively. The color contrast in optical micrographs is enough to identify the least frequent occurrence of contiguous Fe₂Mo/Cr₂N even in N07, the steel with the lowest nitrogen concentration in the current study.

Yet another significant observation from the study is that the absence of stand-alone Cr₂N precipitates in all steels. The Fe₂Mo forms in all samples while the Cr₂N evolves in the compositionally favorable interface. Thus, with nitrogen concentration, the probability of favorable interfaces of Fe₂Mo/Matrix for the formation of contiguous Fe₂Mo/Cr₂N increases and hence the number density. Prolonged aging aids chemical enhancement in both Fe₂Mo and Cr₂N by adding nickel and manganese/carbon, respectively. The stoichiometry of the precipitates can be represented as (Fe, Ni)₂Mo/(Cr, Mn)₂(N, C).

Morphological derivatives of M₂₃(C, N)₆ precipitates in steels

The study shows M₂₃(C, N)₆ type carbo-nitrides evolving in grain boundaries and grain interior. The peculiarities of grain boundary carbides like size, shape, morphology, and crystallographic orientation depend on the nature of grain boundaries. Along low energy grain boundaries, the precipitate’s growth is tangential to the interface, elongated up to ~1 µ with ~300-nm-thickness. These carbides have a cube-on-cube orientation relationship with one of the grains on either side, which facilitates the best possible arrangement to minimize the interfacial energy with the least coherency strain. Each M₂₃C₆ carbide exists with a similar orientation relationship with the matrix [43]. In contrast, carbides evolve in high angle boundaries are big as ~1–2 µm and have an irregular shape. A high strain field in the boundary causes incoherent interfaces. In twin boundaries, cube-shaped carbides of ~200 nm form on either side of the boundary with a cube-on-cube orientation relationship.

Intragranular M₂₃(C, N)₆ precipitates have numerous morphological varieties. Primary stringers and secondary stringers are the major ones as discussed in previous sections. By comparing the optical contrast of stringers with twin planes, the growth plane is identified as (111) (the twins and stringers
are parallel). To find the growth direction of $M_{23}(C, N)_6$ stringer on $\{111\}$ plane, two major possibilities has to be analyzed: (a) twin direction of $\{111\}$ plane i.e., $<112>\gamma$, and (b) slip direction of $\{111\}$ plane i.e., $<110>\gamma$. The analysis is based on the first principle models predicting the ORs (orientation relationships) and the corresponding habit plane with matrix $[44–47]$. Accordingly, the criteria for the formation of low energy interface between two phases are: (a) have a fully or partially coherent orientation relationship that reforms morphology, and (b) the matching atom rows should be close-packed or nearly close-packed $[48]$. In the present scenario of phases with cubic symmetry, $\gamma$ matrix ($a_c = 3.56 \, \text{Å}$, Fm-3 m) and $M_{23}(C, N)_6$ precipitate ($a = 3a_c$, $c = 10.67 \, \text{Å}$, Fm-3 m) have cube-on-cube orientation relationship where all planes and directions are parallel, hence the conditions are valid. As per the first criteria, morphology/growth directions of precipitates are consistent with the degree of mismatch at precipitate-matrix interfaces $[49]$. Minimum mismatch, hence favorable interfacial energy attains by the parallelism between the densely packed planes and directions, i.e., $\langle111\rangle/\langle110\rangle\gamma$. For fcc, the twin direction, $<112>\gamma$ is the least populated direction and undesirable for the growth of precipitates. By the logical conclusion, the preferred growth plane and direction can be chosen as $\langle111\rangle/\langle110\rangle\gamma$, where six crystallographic variants (multiplicities of $<110>$) are allowed for $M_{23}(C, N)_6$ primary and secondary stringers.

The presence of both primary stringers and secondary stringers of $M_{23}C_6$ have been reported in aged high alloyed high carbon (0.1–0.2%) steels by using transmission electron microscopy $[20, 50, 51]$. Straight and intermittently curved primary stringers of length 10–20 μm are visible occasionally in the images. The authors have predicted the growth direction of stringer lie along $<112>\gamma$ from the trace analysis of stereographic projection. However, in the present study, the experimental evidence is given for the dense plane and direction, $\langle111\rangle/\langle110\rangle\gamma$, which is the most favorable growth plane and direction. The cluster of preferentially grown laths has been described in the literature as continuous sheet or thick plates are grown parallel to $\{111\}$ planes, coherent boundary planes like twin boundaries $[20]$. As per the literature, yet another lamella of $M_{23}C_6$ grown on $\{111\}$ planes nucleated on non-coherent twin boundaries $[20, 50, 52]$. In various alloy systems other than steel also show the formation of stringer morphology for $M_{23}C_6$ including Alloy 617 near the grain boundary regions $[53]$. Diffraction contrast imaging in transmission electron microscopy is carried out to emphasize the directional preferences and variant selections of $M_{23}(C, N)_6$ demonstrated by optical microscopy as seen in Fig. 11a-c. The isolated cube, secondary stringer, and cluster of laths are imaged. The cluster of laths is not revealed by optical microscopy; might be due to the smaller size of laths. Each lath is packed on a common strand and is grown towards $<110>\gamma$ direction with cube-on-cube orientation relationship with the matrix. It has to be mentioned that it is tricky to get imaged a lath cluster or a precipitate stringer of 5-μm-length with preferential growth from an electron transparent film of $<100>$-nm-thickness. It is only possible if the grains with precipitates are aligned perpendicular to $<110>\gamma$ direction, the viewing direction. TEM bright-field image of secondary stringer (Fig. 11b) reveals the morphology of stringers as ‘string of cubes of $M_{23}(C, N)_6$’. The direction of growth of stringer establishes as $<110>\gamma$ experimentally by diffraction analysis. This can also be confirmed from the shape of these precipitates seen in diffraction contrast images, which are perfectly cuboidal with cube-on–cube orientation relationship with the matrix. The image is projected along $[001]_\gamma$ direction and $<110>\gamma/M_{23}C_6$ direction can be easily distinguished by its cubical geometry.

In conclusion, four varieties of $M_{23}(C, N)_6$ precipitate morphology are observed as shown in the schematic diagram (Fig. 11d): (1) isolated cube-shaped precipitates dispersed all over the matrix, (2) Primary stringers: also called strings of cubes or string formation by an edge to edge contact of the cube-shaped precipitates preferentially grown in $\langle111\rangle/\langle110\rangle\gamma$, (3) Secondary stringers: clusters of preferentially grown branched precipitates along $\langle111\rangle/\langle110\rangle\gamma$ from a common strand and (4) clusters of preferentially grown laths along $\langle111\rangle/\langle110\rangle\gamma$. There are three preferential directions in $\langle111\rangle$ plane suggesting the probability of three-dimensional formation of secondary stringers and lath clusters in the system. Two variants for primary stringers and secondary stringers are imaged by optical microscopy further six crystallographic variants are predicted by logical analysis in experimental results. Thus, a comprehensive analysis of directional preferences of growth and variant selections of
primary and secondary stringers is thoroughly done in this study.

Precipitate sub-structure emerged with nitrogen content tailoring mechanical properties

Following the identification of precipitates by unique color contrast, quantification of each precipitate has been carried out by selecting unique color components by image processing as given in Table 2. Area fraction of precipitates in N07 is 1.6% which increases substantially up to 12.5% for N22 steels. The percentage of area fraction for contiguous Fe$_2$Mo/Cr$_2$N is negligible for N07 and N11 samples, but for N14 and N22 steels, the values are 0.34% and 2.7%, respectively. It is interesting to realize that N14 steel shows an abrupt variation in contiguous

**Figure 11** Morphological derivatives of M$_{23}$(C, N)$_6$ precipitates in SS 316LN. Diffraction contrast TEM images resolve a isolated cube, b Cluster formation of strings of cubes/stringers of M$_{23}$(C, N)$_6$; c laths of M$_{23}$(C, N)$_6$; d Schematic diagram shows four derivatives of intragranular M$_{23}$(C, N)$_6$ precipitates: (1) isolated cube-shaped precipitates, (2) Primary stringers: string formation by an edge to edge contact of cube-shaped precipitates preferentially grown in $\{111\}/ <110> \gamma$, (3) Secondary stringers: clusters of preferentially grown primary stringers as branches along $\{111\}/ <110> \gamma$ from a common strand and (4) clusters of preferentially grown laths along $\{111\}/ <110> \gamma$. Crystallographic variants have been identified experimentally for primary stringers and secondary stringers.

**Table 2** Quantification of precipitates in SS 316LN

| Sample | Area fraction (%) | Contiguous Fe$_2$Mo/Cr$_2$N |
|--------|------------------|-----------------------------|
| N07    | 1.6 ± 0.205      | 0.0001 (from single image)  |
| N11    | 2.7 ± 0.194      | 0.005 (from single image)   |
| N14    | 5.2 ± 0.814      | 0.34 ± 0.042                |
| N22    | 12.5 ± 1.44      | 2.7 ± 0.386                 |
precipitation. In N22, most of the Fe$_2$Mo (green) precipitates form contiguously with Cr$_2$N.

Apart from the rise in total precipitate density, the evolution of derivatives of intra-granular M$_{23}$(C, N)$_6$ precipitates vary with nitrogen content (summarized in Table 3). Isolated cubes, common in all steels line up and transform into primary stringers in N07, N11, and N22 steels. Adding excess nitrogen introduces clusters of stringers and laths, as seen in the N22 sample. The exceptionality shown by N14 is the absence of primary stringers, even though it occurs in lower concentrations, which implies the composition is energetically favorable for the formation of contiguous Fe$_2$Mo/Cr$_2$N than M$_{23}$(C, N)$_6$ stringers. A similar trend has been seen in aged duplex stainless steel, where the growth of M$_{23}$C$_6$ ceases and that of Cr$_2$N continues as aging progress [54].

The primary stringers present in N07, N11, and N22 samples lie in {111} planes along $<110>$ direction. Crystallographic analyses on light optical micrographs and TEM images confirm the presence of six variants of primary stringers on $<110>$ directions by imaging a minimum of 2 variants in each grain. The number density measurements from the two-dimensional images of preferentially grown variants may give only a fraction of the actual amount. However, the comparison is possible since there is a significant difference within each sample. Most of the intra-grain amaranth precipitates elongate in the N22 sample. For higher nitrogen concentration, M$_{23}$(C, N)$_6$ is more likely to grow as stringers. Also, it has been noted that the number density of stringers is high in nearby regions of boundaries of grains or twins. In N14 steel, stringers are hardly seen, however, the advanced formation of Fe$_2$Mo/ Cr$_2$N co-precipitation indicates the preference of chromium for switching from M$_{23}$(C, N)$_6$ stringer to Cr$_2$N precipitates with adequate nitrogen content.

In our previous study, a rise in hardness with nitrogen concentration is noticed from N07 to N14, however N22 steel doesn’t show any significant variation [16]. The total increase in precipitate density, coarsening of incoherent precipitates (Fe$_2$Mo/ Cr$_2$N), and cluster formation of coherent M$_{23}$(C, N)$_6$ stringers instigate depletion of strengthening elements in the matrix leading to the anomalous change in hardness of N22 steel. The mechanism of dislocation gliding through M$_{23}$(C, N)$_6$ precipitate enhance the reverse effect in hardness (diffraction contrast imaging in TEM under two-beam dynamical condition is shown in Fig. 11a). The image depicts dislocation pileups in a slip band that smoothly glides through M$_{23}$(C, N)$_6$. The continuity of dislocation lines on the interface indicates a negligible strain field at the boundary, hence proving the extent of coherency between phases. The excess formation of primary and secondary stringers in N22 might contribute to the hardness reduction. Additionally, the size attained by the clusters of cubes is very large; up to hundreds of micrometers, which might impart detrimental effect to the system.

The ultimate tensile strength increases with the increase in nitrogen content [16]. Excess addition of interstitial elements results in the formation of substantial secondary phases while aging gives a precipitate strengthened effect to the system. Hence, the mechanical properties of the steels with varying nitrogen content can be interpreted more relatively with precipitate strengthening effects than interstitial effect. To summarize, the study demonstrates the role of nitrogen as a precipitate strengthener than an interstitial strengthener in SS 316LN during prolonged aging.

**Table 3** Derivatives of intra-granular M$_{23}$(C, N)$_6$ precipitates in SS 316LN

| Sample | isolated cubes | Primary stringers | Secondary stringers | clusters laths |
|--------|----------------|-------------------|---------------------|----------------|
| N07    | ✓              | ✓                 | ×                   | ×              |
| N11    | ✓              | ✓                 | ×                   | ×              |
| N14    | ✓              | × (rare)          | ×                   | ×              |
| N22    | ✓              | ✓                 | ✓                   | ✓              |

Primary stringers are more in comparison with isolated cubes
Conclusions

- Optimal preparation methods in vibratory polisher are employed to reveal the microstructure in long-term aged SS 316LN with varying nitrogen content by bright field color contrast in optical imaging.
- \(\text{M}_{23}(\text{C, N})_6\) and \(\text{Fe}_2\text{Mo}\) form abundantly in all steels, whereas, \(\text{Cr}_2\text{N}\) is largely identified in higher nitrogen-containing samples (N14 and N22). The contiguity of \(\text{Fe}_2\text{Mo}/\text{Cr}_2\text{N}\) precipitates is characterized with diffraction contrast imaging in TEM and quantified by light microscopy.
- The distribution of morphological derivatives of \(\text{M}_{23}(\text{C, N})_6\) with nitrogen content has been exclusively categorized by optical imaging as four intra-granular varieties: (1) isolated cubes, (2) primary stringers (3) secondary stringers, and (4) clusters of laths. The preferential growth (\(\langle 111\rangle/\langle 110\rangle\)) and crystallographic variants for stringers and laths are demonstrated. Hence, the versatility of the optical microscopy together with vibratory polishing techniques has been highlighted.
- The secondary stringers and clusters of laths are present in the high nitrogen sample (N22).
- The dislocation gliding through \(\text{M}_{23}(\text{C, N})_6\) clusters in the N22 sample can be attributed to the hardness reduction.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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