Microstructural engineering of medium entropy NiCo(CrAl) alloy for enhanced room and high-temperature mechanical properties

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ABSTRACT

This work demonstrates the development of a strong and ductile medium entropy alloy by employing conventional alloying and thermomechanical processing to induce partial recrystallization (PR) and precipitation strengthening in the microstructure. First, the cold working of homogenized alloy resulted in a highly deformed microstructure. On annealing at 700 °C, B2 ordered precipitates heterogeneously nucleate on the highly misoriented sites. These B2 promotes particle stimulated nucleation (PSN) of new recrystallized strain-free grains. The migration of re-crystallized grain boundaries leads to discontinuous precipitation of L12 ordered regions in highly dense lamellar structures. We also observe near-spherical L12 precipitates in the non-recrystallized grains. Atomic-scale compositional analysis reveals a significant amount of Ni confined to the Phase Boundary (PB) regions between B2 and L12 precipitates, indicating Ni as a rate-controlling element for coarsening the microstructure. On 20 h of annealing, the alloy comprises a composite microstructure of recrystallized and non-recrystallized grains, B2 particles at the grain boundaries (GBs), and coherent L12 precipitates inside the grains. The microstructure results in a 0.2% yield stress (YS) value of ~1060 MPa with ~25% elongation at ambient temperature and retains up to ~910 MPa at 670 °C. Examination of deformed microstructure reveals excessive twinning, formation of stacking faults, shearing of L12 precipitates, and accumulation of dislocations at around the B2 precipitates and GBs attributed to high strain hardening of the alloy.

1. Introduction

Design of single-phase alloys by mixing the multiple principal elements in equimolar or near equimolar ratios, showed a great promise with excellent mechanical properties at room and cryogenic temperatures [1–3]. These alloys are characterized by four core effects: (1) high entropy, (2) lattice distortion, (3) sluggish diffusion, and (4) cocktail [4–7]. High entropy increases the phase stability of single-phase over intermetallic phase formation. Lattice distortion due to atomic size mismatch induces hardening by resisting dislocation motion on loading, sluggish diffusion was proposed to retard the phase transformation kinetics, and the cocktail is related to the synergistic response with improved physical and mechanical properties. In particular, the model face-centered-cubic (fcc) high entropy alloy (HEA) “FeCoNiCrMn” shows a substantial improvement of yield strength, ductility, and toughness as the temperature reduces up to cryogenic conditions [8]. However, at room temperature, the alloy yields at a very low stress (0.2% YS) value of 200 MPa, and by reducing the grain size (from 155 μm to 4.4 μm), the 0.2% YS increases up to only 350 MPa [9,10]. As the temperature increases, the 0.2% YS drops drastically, for example, by ~30% at 400 °C [11]. Later, strengthening by dispersion of coherent L12 precipitates by adding Ti and Al to a similar single-phase fcc FeCoNiCr alloy was demonstrated that increased the 0.2% YS up to 645 MPa at room temperature with ~39% plasticity [12]. The microstructure also contains an additional L21 Heusler-like phase, mainly at the GBs. Here, the strengthening L12 precipitates are only stable up to 550 °C, while at higher temperatures, the precipitates decompose, and ordered B2 precipitates appear inside the grains and at the GBs [13]. Cu addition improved the stability of L12 precipitates up to 700 °C (for 50 h), where Cu-rich clusters in the matrix act as heterogeneous nucleation sites for the L12 precipitates [14]. But at higher temperatures, Cu-rich needle shape precipitates dominate the microstructure. Hence, these alloys might have limitations to be used at such high temperatures. The reason for the L12 precipitate instability might be the presence of Fe in the alloys, which will be discussed in detail later.

On the other hand, NiCoCr alloy (medium entropy configuration) shows a better combination of mechanical properties (yield strength, ductility, and fracture toughness) than quaternary or quinary alloys at room and cryogenic temperatures. This was attributed to the reduction of stacking fault energy (by ~25%), which is proposed to resist cross-slip and promote nano-twinning as the strain accumulator during deformation [15]. As for MEA, the feasibility of forming L12 precipi-

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tates has been recently exploited by adding Al and Ti [16–18]. An increase in Y.S. by ~ 70% (up to 750 MPa) is reported [18]. However, studies on their high-temperature properties are limited [17,19]. The H/MEA were also highly sensitive towards partial recrystallization (PR) that led to the formation of hierarchical microstructures and offered a new thermo-mechanical processing platform for designing alloys overcoming the strength-ductility tradeoff at room temperature [20,21].

In this work, a Ni$_{0.33}$Co$_{0.33}$Cr$_{0.33}$ equiatomic MEA was chosen, and some part of the Cr was replaced by Al having the composition Ni$_{0.33}$Co$_{0.33}$Cr$_{0.33}$ (here onwards NCC) and Ni$_{0.33}$Co$_{0.33}$Cr$_{0.33}$Al$_{0.09}$ (here onwards NCCA) were melted in the form of 50 μ buttons using a vacuum arc melting unit under argon atmosphere. The constituent elements have 99.99% purity. The alloys were remelted 5 to 6 times by flipping after each cycle of melting for homogeneity. The buttons were subsequently cast in the form of a slab (70 mm x 20 mm x 10 mm) using a water-cooled copper split mold in a vacuum casting unit under argon atmosphere.

2. Experimental

2.1. Alloy preparation

Alloy ingots with nominal compositions (all in at.%) of Ni$_{0.33}$Co$_{0.33}$Cr$_{0.33}$ (here onwards NCC) and Ni$_{0.33}$Co$_{0.33}$Cr$_{0.33}$Al$_{0.09}$ (here onwards NCCA) were melted in the form of 50 μ buttons using a vacuum arc melting unit under argon atmosphere. The constituent elements have 99.99% purity. The alloys were remelted 5 to 6 times by flipping after each cycle of melting for homogeneity. The buttons were subsequently cast in the form of a slab (70 mm x 20 mm x 10 mm) using a water-cooled copper split mold in a vacuum casting unit under argon atmosphere.

2.2. Thermomechanical processing

The cast slabs were homogenized (H) at 1200 °C for 20 h in a tubular furnace maintained under a vacuum of 10$^{-5}$ mbar followed by water quenching. The homogenized samples were cold-rolled (C) to a reduction ratio of 70% and subsequently annealed (A) at a temperature of 700 °C for 20 h, followed by water quenching. This thermomechanical heat treatment will be called HCA (Homogenization (H) + Cold working (C) + Annealing (A)) in the rest of the manuscript. The microstructural stability was also evaluated by annealing at 700 °C for up to 500 h.

2.3. Microstructural characterisation

Identification of phases for the annealed samples was conducted using an X-ray diffractometer (XRD, Rigaku) operated at room temperature with Cu Kα source equipped with Johannson optics that eliminates the Ka2 and Kβ components. The phase transformation temperatures were determined in a differential scanning calorimeter (DSC, STA449F3 NETSCH). DSC samples weighing 50 mg were cut from the alloy after HCA thermomechanical processing and heated at a 10 K/min rate under argon atmosphere till 1450 °C and cooled at the same rate to room temperature.

After each experimental step, the microstructures were characterized by using a scanning electron microscope (SEM, Helios Nanolab) equipped with a field-emission-gun source (FEG). Electron backscattered diffraction (EBSD) patterns were recorded in Gemini SEM450 (Carl Zeiss) equipped with a velocity detector using a step size of 0.1μm. For SEM and EBSD analysis, samples were prepared following a standard metallography technique using Si grit papers and final polishing in a Vibro-polisher (VibroMet Buehler made) with colloidal silica suspension of 200 nm particle size. The high temperature deformed samples were also investigated by controlled electron channeling contrast image (cECI) using a Zeiss SEM (Carl Zeiss) equipped with a Gemini field emission gun electron column operated at 30 kV with a probe current of 5 nA. The working distance was kept at ~ 6 mm during imaging. First, the deformed region of interest (ROI) on the bulk sample was identified, and the crystallographic orientation of the region was measured by EBSD. A pole figure was generated for the ROI using orientation imaging microscopy software (OIM). The exact orientation was generated in a single crystal software to access the Kikuchi pattern for the particular orientation directly. Using single-crystal software, we obtained the stage tilt and rotation values required for the ROI to be in two-beam conditions. The microscope stage was aligned according to the measured values, and imaging was done using a backscattered electron detector (BSE).

Electron diffraction analysis was performed using a transmission electron microscope (TEM, Tecnai T20) operated at 200 kV. High-resolution imaging was done in an aberration-corrected TEM in STEM mode (Titan Themis) operated at 300 kV. Atomic-scale compositional analysis was performed by atom probe tomography (APT) in LEAP 5000XHR ( Cameca instruments) equipped with a reflectron. An ultraviolet picosecond laser pulse with a pulse repetition rate of 125 kHz and pulse energy of 55 pJ was used for field evaporation. The base temperature of needle specimens was maintained at 60 K with a target detection rate of 5 ions per 1000 pulses.

The APT data analysis and reconstruction were performed using the IVAS PRO software package. TEM and APT specimens were prepared by standard site-specific in-situ lift-out protocols [24] using a dual-beam SEM/focused ion beam (FIB) instrument (ThermoFisher Scios) operated at 30 kV. APT specimens from the deformed regions were also prepared directly from the TEM lamella after the TEM experiments from the exact location. A final cleaning of TEM lamella and the APT needles was carried out at 2 kV with an 8 pA current to remove the damaged regions caused during prior Ga$^+$ ion milling.

2.4. Mechanical properties

Room temperature tensile and high temperature compressive mechanical properties were evaluated using an Instron 5967 UTM (Ultimate Tensile Machine) loaded at a constant strain rate of 10$^{-3}$ s$^{-1}$. Dog-bone shape flat specimens were cut from the alloys after HCA thermomechanical heat treatment for tensile testing, as per the ASTM standard E8. Digital-image-correlation (DIC) method was used to measure the strain of the samples during tensile loading (see supplementary figure 1). Cylindrical samples of 3 mm diameter and 4.5 mm height (height/diameter ratio = 1.5) were also cut from the alloy for a high-temperature compression test. A minimum of 3 samples were tested for both tensile and compressive testing. The hardness values were measured using a Vickers microhardness tester (FutureTech, FM-800) by using a load of 0.5 kg.

3. Results

3.1. Mechanical properties

Fig. 1(a) shows uniaxial tensile test engineering stress-strain curves for both NiCoCr (NCC) and NiCoCrAl (NCCA) MEA alloys after HCA thermomechanical heat treatment. The tensile yield strength (0.2% YS) and ultimate tensile strength (UTS) for NCC alloy are measured to be 450 ± 15 MPa and 830 ± 25 MPa, respectively, with the elongation to failure 47 ± 6%. In comparison, the NCCA alloy show 0.2% YS and UTS of 1060 ± 10 MPa (higher by ~135%) and 1335 ± 5 MPa (higher by ~61%), maintaining a ~ 25 ± 3 % elongation to failure. Fig. 1(b) shows an Ashby plot between UTS and elongation that compares the values of NCCA alloy (red star) with Fe containing NiCoCrMn based HEA
and other critical engineering alloys. It demonstrates a unique place with a good combination of mechanical properties at room temperature. Further, the high-temperature properties of NCCA alloy are evaluated using compression tests up to 770 °C.

Fig. 1(c) shows a comparison of 0.2% YS values vs. temperature for NCCA alloy with a few earlier reported values for HEA and some commercial Ni-based and Co-based superalloys. The 0.2% YS for NCCA shows decreasing tendency as the temperature increases and maintains a value of 910 ± 8 MPa at 670 °C, comparable to Ni-base MAR-M-247 superalloy and superior to even some of the refractory HEAs. At 770 °C, the value reduces to 600 ± 10 MPa. For microstructural stability at high temperature, the NCCA alloy was annealed at 700 °C up to 500 h, and hardness was taken at room temperature after different time intervals. The temperature selection to examine stability was based on DSC experiments which will be discussed later. The hardness variation with the annealing time, Fig. 1(d), shows the negligible change in the values indicating the mechanical stability of the alloy.

3.2. Microstructural analysis

Now, we detail the microstructure features of NCCA alloy in correlation with the obtained properties. Fig. 2(a & e) compares secondary electron (SE) micrographs of NCC and NCCA alloys after HCA thermo-mechanical heat treatment. NCC alloy is fully recrystallized with fine equiaxed grains of average size ~ 6 μm. Fig. 2(b) shows the electron backscattered diffraction (EBSD) grain orientation map from a region of the alloy. In contrast, NCCA alloy is partially recrystallized (PR); see Fig. 2(d) for the overlaid image quality (IQ) and grain orientation map. It contains ~70% recrystallized zones of fine grains (1.5 to 2 μm) and non-recrystallized zones of coarse grains (several tens of micron sizes (marked in red arrow)). Fig. 2(f) shows a higher magnification micrograph that reveals two kinds of second phase precipitates formed along the grain boundaries (GBs) and interior of the recrystallized grains.

X-ray diffraction (Fig. 2(c)) analysis for the NCCA alloy after homogenization (H) confirms the presence of a single fcc phase throughout the microstructure. However, after HCA, additional diffraction peaks correspond to B2 ordered structure appear. From the microstructure in Fig. 2(e and f), the B2 peaks might be attributed to the precipitates at the GBs. The fine precipitates inside the recrystallized grains are in the lamellae form typical of discontinuous precipitation. Note that the lamellae precipitates are not present in non-recrystallization zones (see Fig. 2(f) indicated by red arrows), indicating their discontinuous formation during the migration of GBs on recrystallization [45]. The morphology of the lamellae structure shows the spacing is relatively higher adjacent to the GBs than the interior of the grains.
Fig. 2. Microstructural analysis after HCA thermomechanical heat treatment for (a-b) NCC (d-h) NCCA alloys: (a) SEM image and (b) EBSD IPF map for NCC alloy. (d-f) SEM images and overlay image quality (IQ) EBSD IPF map for NCCA alloy. (c) Comparison of XRD patterns of NCCA alloy after homogenization (H) and after HCA. Darkfield (DF) images highlighting (g) a B2 ordered precipitate located at a GB triple junction and (h) L1₂ ordered precipitates from a lamellae region inside of a recrystallized grain in NCCA alloy.

Fig. 2(g) shows a darkfield (DF) micrograph of a precipitate formed at a GB triple junction. The corresponding diffraction pattern is shown as an inset and can be indexed as the [001] pattern of the B2 ordered crystal structure. Similarly, the diffraction pattern from the interior of a recrystallized grain (see inset Fig. 2(h)) indicates the presence of additional superlattice reflections along with the primary fcc reflections in the [001] oriented pattern. These reflections are attributed to L1₂ ordering, and the darkfield from one of the superlattice reflections highlights the ordered regions in the form of lamellae structure, Fig. 2(h). The average spacing between the adjacent ordered regions is ~29 nm.

Additionally, we also observe twins in the recrystallized grains of NCCA alloy that are attributed to the growth accidents at the migrating GBs during recrystallization [46,47]. Fig. 3(a) shows a BSE image centered on one such twin in a recrystallized grain. The lamellae structure is also present in the twinned region, as also shown in the subsequent TEM analysis. Fig. 3(b) shows a pair of BF and DF (taken from a twinning spot) images taken along the [110] zone axis (corresponding DPs are presented on the left side), highlighting the twinned region in the matrix. The DP from the twin/matrix indicates the twinning plane as [111]. Fig. 3(c) shows the DF images taken from the 001 L1₂ superlattice spots of both twinned and matrix region that highlights the respective lamellae structure. Fig. 3(d) shows the cut section of the exact same region (green checked box) centered on the interface. On overlapping the images (Fig. 3(e)), we observe discontinuity of the lamellae structure at the interface even though they have common [111] plane (see DP from the interface). This suggests that the discontinuous precipitation is preceded by twinning during the migration of the reaction front.

Fig. 4(a) shows an atom probe reconstruction of a needle specimen with the distribution of Al (blue) and Cr (golden) atoms taken from a phase interface between B2 and lamellae structure. The top part of the reconstruction corresponds to B2 precipitate, while the L1₂ ordered precipitates are shown by the iso-composition surfaces delineated with a threshold value of 26.5 at.% Ni. The composition profiles across B2 and the adjacent grain fcc matrix (Fig. 4(b)) reveal a high amount of Ni (~46 at.%) and Al (~40 at.%) with lower content of Co (~11.5 at.%) and Cr (~2.5 at.% in the precipitate. The diffraction analysis and compositional data indicate these are B2-(Ni,Co,Cr)Al precipitates. The compositional profiles across an L1₂ ordered precipitate (Fig. 4(c)) in the lamellae region show higher content of Ni and Al in the precipitate relative to the adjacent matrix. The compositional values, as shown in Table 1, indicate these are (Ni,Co,Cr)₂Al L1₂ ordered precipitates. The partitioning coefficient (Kᵢ) values across the precipitate-matrix interface for each solute (i) are calculated using the relation 

\[ Kᵢ = \frac{Cᵢ^P}{Cᵢ^M} \]

where, Kᵢ is the partitioning coefficient of element i. Cᵢ^P and Cᵢ^M are the compositions of element i in the precipitate and matrix. The Kᵢ values are also listed in Table 1. Ni and Al show strong partitioning to the precipitates (KᵢNi = 2.4 and KᵢAl = 4.8), whereas Co and Cr partition to the matrix (KᵢCo = 0.41, and KᵢCr = 0.17). Similar partitioning behavior of these solutes was observed in several Ni-based, Co-based, and HEA superalloys responsible for their excellent high-temperature mechanical properties [48–53]. Similarly, we also get evidence of near-spherical L1₂ ordered precipitates in a non-recrystallized grain, as shown from the APT analysis in Fig. 4(d, e).

3.3. High-temperature stability

To know the stability of these L1₂ ordered precipitates, DSC was carried out for NCCA alloy. Fig. 5(a) shows the DSC plot during the heating...
Fig. 3. (a) A BSE SEM image of NCCA alloy centered on a twinned region of a recrystallized grain. and (b-c) A pair of BF and DF images highlighting twin and lamellae structure in the matrix and twinned region. (e) Overlap of cut section of DF images (green checkered boxes) from the twin/matrix interface showing the discontinuity in the lamellae structure across the interface.

Fig. 4. (a) An APT reconstruction with the distribution of Cr and Al atoms across a B2 precipitate and lamellae structure. Composition profiles across (b) B2 and (c) lamellar L12 precipitate. (d) APT reconstruction for a needle specimen taken from a non-recrystallized grain and (e) compositional profile across one of the L12 precipitates.
cycle that indicates a slope change near 800 °C that can be attributed to the dissolution of L1₂ precipitates in the matrix. Hence, we choose 700 °C for evaluating the stability of the microstructure of NCCA alloy by annealing up to 500 h. Fig. 5(b) and (f) show the SEM micrographs after 250 h and 500 h of annealing, respectively. The recrystallisation fraction increases from 70% for 20 h to 91% for 250 h (Fig. 2(d)) and fully recrystallized after 500 h (Fig. 2(h)). In addition, the change in average grain size is not significant (3.4 for 20 h to 5 μm for 500 h). In contrast, the NCC alloy is fully recrystallized with the same HCA thermomechanical heat treatment (20 h).

In the grain interior, the L1₂ precipitates also remain stable without any evidence of decomposition. However, the average lamellae spacing increased from 28 nm for 20 h to 150 nm for 500 h annealed sample due to discontinuous coarsening (DC). Compositional analysis from a lamellae region (Fig. 5(e)) for the 250 h sample reveals no significant change in the partitioning behavior of solutes (Table 1) across the L1₂ precipitate/matrix interface. Additionally, the average size of B2 precipitates increases from 320 nm (20 h) to 630 nm (for 250 h) and 690 nm for 500 h and are also confined only to the GBs, i.e., we couldn’t observe them in any of the grain interiors. The volume fraction of B2 precipitates increases from ~5% for 10 h to ~ 8% for 20 h to ~12% for 250 h and ~15% for 500 h, indicating they were in the growth regime and may about to coarsen after 500 h. Hou et al. [54] showed the occurrence of Ostwald ripening of B2 precipitates on annealing at a higher temperature of 1000 °C in CoCrNiFeAl₀.₄₅ high entropy alloy.

### 3.4. Deformation structure

Fig. 6(a) shows the plots between the work hardening rate vs. (σ - σ_y) for NCC and NCCA alloys. It indicates NCCA offers a higher work hardening rate within its uniform plastic regime (<23% true strain, according to Consid’ere instability criteria [55]). The room temperature tensile deformed NCCA alloy was also investigated by EBSD kernel average misorientation (KAM) map, as shown in Fig. 6(b). The map shows a high degree of intergranular rotation and development of local misorientations near the GBs, indicating the GBs as major stress concentration centers during deformation. Some regions of the GBs have higher stress concentration (marked by arrows) which is expected to be the B2 precipitate locations. STEM HAADF analysis (Fig. 6(c, d)) on the deformed sample reveals a significant amount of deformation twinning (see twinning spots in the diffraction pattern taken along [110] zone axis) and the presence of stacking faults (SFs) at the interior of recrystallized grains in the microstructure as shown in a high-resolution HAADF STEM image (Fig. 6(d)).

Fig. 6(e, f) shows a pair of TEM brightfield (BF) and DF images from the twinned location marked as a red checked box in Fig. 6(c). The diffraction pattern shows twinning spots and the superlattice spots from L1₂ ordering. The DF image is taken from one of the superlattice spots, highlighting the effect of deformation on the L1₂ precipitates. We could see extensive shearing of the precipitates (indicated by red dashed lines and white arrows) by the movement of dislocations. An APT specimen of the twinned location was prepared from the same TEM lamella. Fig. 6(g) shows the APT reconstruction with the distribution of Al and
Cr atoms. Ni 22.5 at.% iso-compositional interfaces represented the γ′ precipitates. We observe the cutting of γ′ lamellae and relative displacement of the cut γ′ parts by the shearing events (marked by black arrows). A 3-dimensional visual is also provided as a supplementary video 2. cECCI was carried out for the sample that was compressively deformed at 670 °C. A deformed region in a recrystallized grain was located with an orientation close to the [110] zone axis (Fig. 7(a, b)). A near two-beam condition for the ROI was achieved with \( g = 1 \overline{1} 1 \) (where \( g \) is the diffraction vector) by tilting and rotation of the sample stage in SEM (see the experimental section for details). The corresponding stereogram is also shown in Fig. 7(c). Fig. 7(d, e) shows the recorded cECC images from the same ROI. The images clearly show channeling contrast from the defects that appear brighter to the dark surrounding regions. We observe sub-structure boundaries whose traces lie on \( \{111\} \) planes. Additionally, the dislocations are piled at these sub-structure boundaries and around the B2 precipitate (see inset in Fig. 7(d)).

### 4. Discussion

The above experiments highlight the sensitivity of an MEA towards alloying (Al addition) and thermomechanical processing (HCA) with the microstructure comprising recrystallized and non-recrystallized grains with L1₂ ordered strengthening precipitates and B2 ordered precipitates at GBs that resulted in a good combination of mechanical properties. We also observe a decrease in recrystallization kinetics for the NCCA alloy as compared to the NCC alloy. First, we discuss the elements responsible for the slower recrystallization kinetics in NCCA alloy.

#### 4.1. Recrystallization

NCCA alloy was annealed in a state of supersaturated solid solution and plastically deformed. Hence, the microstructure will have a tendency to exhibit both recrystallization and second-phase precipitation. After annealing at 700 °C for 20 h, we observe continuous precipitation of near-spherical L1₂ precipitates in non-recrystallized grains while discontinuous precipitation of L1₂ precipitates in lamella structure in recrystallized grains. Fig. 8(a) shows a BSE image of a non-recrystallized grain with a large amount of deformation-induced planar slips. We could also observe a few B2 precipitates inside the grains and along with the coherent near-spherical L1₂ precipitates (Fig. 4(d)), without any evidence of recrystallization around them. This indicates the system prefers earlier nucleation of precipitates rather than new grains, as also observed in earlier studies [56]. The B2 precipitates are incoherent and might be heterogeneously promoted to form on the highly deformed and misoriented sites in the non-recrystallized grains [57,58].

On further annealing, these B2 precipitates grow and induce additional volumetric strain around the precipitates in the surrounding grain. This creates additional strain and orientation gradients that can act as nucleation sites for the new recrystallized grains, Fig. 8(b). This is also evidenced from the KAM map (Fig. 8(c) and EBSD IPF map (Fig. 8(d)) of the same region from a non-recrystallized grain containing few B2 precipitates. The KAM map shows a relatively higher strain around the B2 precipitates to the surrounding grain. The EBSD IPF map reveals nucleation and growth of a recrystallized new grain with negligible strain inside. The B2 precipitates also pin the GB. This nucleation event is called particle stimulated nucleation (PSN) of new grain [56]. Hence, the distribution of B2 precipitates in the non-recrystallization grains is proposed to control and promote finer size distribution of the new recrystallized grains. Similar observations were made in CoCrFeNiAl high entropy alloy by the presence of B2 precipitates [54]. Further, when the grain boundaries (GBs) of the nucleated new grains migrate, simultaneously, discontinuous precipitation [45] of strengthening coherent L1₂ ordered regions takes place in the form of lamellae structure, as shown in Fig. 2(b and e). Discontinuous precipitation of L1₂ ordered regions during recrystallization was also observed in FeNi-CoCrAl HEA [29,59] and Ni-base superalloys. Several mechanisms were proposed on the discontinuous precipitation depending on the alloy system. In the present case, the most relevant is the mechanism proposed...
by Williams and Edington [60] that was observed during grain boundary migration in an Al-Li alloy with the matrix containing spherical coherent L12 Al3Li precipitates. They suggested the precipitates dissolve at the moving grain boundary and reprecipitate behind, i.e., the moving GB leaves behind a supersaturated solid solution region that decomposes to alternate layers of elongated L12 precipitates and solutes lean solid solution matrix. Here the migrating GBs assist the solute redistribution since the GBs are shown as fast diffusing paths for solutes as compared to the bulk lattice. Dissolution of precipitates during the migration of GBs is also observed and reported in several works [61–68]. Hence, the prior presence of precipitates will have an essential role in the recrystallization behavior.

Fig. 9(a) shows the top section of the APT reconstruction (Fig. 4(a)) centered on the phase interface. We plotted composition profiles across B2/L12 and B2/fcc matrix, as shown in Fig. 9(b). The former profile reveals a significant amount of segregation of Ni (up to 63 at.%) at the GB. In comparison, Co and Cr are depleted by up to 8 at.% and 1.5 at.%, respectively, as compared to the adjacent compositions of B2 and L12 precipitate. However, we couldn’t notice any similar segregation of Ni or depletion of Co/Cr at the GB between B2 and adjacent grain fcc matrix. Fig. 9(c) shows the same reconstruction on xz plane viewed from the bottom of the GB that clearly distinguishes the L12 and fcc matrix. We plotted a 2D Ni compositional map of the GB plane for the Ni distribution. We observed in-homogenous distribution, i.e., the segregation of Ni is confined only to the locations where L12 precipitates are nucleated.

Hence, from these atomic-scale observations, we propose rate-limiting diffusional mechanisms that are demonstrated through a schematic in Fig. 9(e).

In the schematic diagram, we have also kept the average composition of all the solutes in the respective phases. During annealing, the B2 precipitate interface advances to the lamellae region and hence needs local diffusion or rearrangement of atoms to obtain the equilibrium B2 composition. We have marked as zone 1 for L12 and zone 2 for fcc matrix regions in the schematic. The solute diffusion directions are also indicated from the relative solute compositions and observed phase boundary segregation behavior. When the interface of B2 advances, say by x distance, Ni will be higher in zone 1 while lower in zone 2 to the required equilibrium concentration in B2. Thus, the excess Ni from zone 1 needs to diffuse to zone 2. The evidence of segregation of Ni at the GB between B2 and L12 indicates that the excess Ni will diffuse along the GB to zone 2. The diffusion will continue to happen until it reaches the required equilibrium Ni concentration in B2. Parallelly, since Al is lower in zone 1 and zone 2 as compared to B2, the Al will be consumed from the lamellar structure to reach the equilibrium Al concentration in B2. Further, both Co and Cr are higher in zone 1 and 2 than the required in B2; hence, they will diffuse away from GB towards the lamellae structure. This is supported by our observation of Co, and Cr depletion near the GB shared between B2 and L12. Overall, this diffusional scheme will result in the growth of the B2 precipitate at the expense of the lamellar structure. This indicates that B2 is relatively more stable than the lamellar structure.
ture which is also shown in the CoCrNiFeAl_{1.5} high entropy alloy [69]. They found destabilization of L1\textsubscript{2} precipitates and are replaced by the coarser distribution of B2 precipitates on annealing at 700 °C for 50 h. In the present case, the solute segregation effects at B2/lamellae phase boundary show the solute diffusivities might be the rate-controlling for destabilizing the lamellae structure during annealing.

Quantitatively, the slower recrystallization kinetics can be explained by considering the migration velocity \( v \) of a GB during recrystallization [70,71], and it is given as \( v = m \times \rho \), where \( m \) is interfacial mobility, and \( \rho \) is net driving pressure acting on the GB. The net driving pressure is resultant of four important forces acting on the migrating GB. The driving forces for migration are (1) a decrease in the free energy per unit volume by the release of elastic stored energy through dislocations (\( P_\text{D} \)) and (2) the chemical driving force for reprecipitation behind the boundary (\( P_\text{C} \)). The obstructing forces are (3) Zener drag (\( P_\text{Z} \)) due to B2 and prior present L1\textsubscript{2} precipitates ahead of the boundary and (4) solute drag (\( P_\text{s} \)) due to the accumulated solute at the moving GB plane. Since the prior present precipitates are dissolving at the migrating boundaries, the Zener pinning by those particles can be neglected. So, the net \( P = (P_\text{D} + P_\text{C}) - (P_\text{Z} + P_\text{s}) \). \( P_\text{D} \) is given by \( P_\text{D} = \frac{\pi \rho m \mu}{4} \) [72]. The \( \rho \) value is considered to be \( 5 \times 10^{-13} \text{ m}^2/\text{s} \), for a typical cold-worked material. Shear modulus (G) is assumed to be 87 GPa for a NiCoCrAl (73) with \( b = 0.252 \text{ nm} \) the length of the Burgers vector. Hence, \( P_\text{D} \) is estimated to be \( 5.4 \times 10^6 \text{ J/m}^2 \). The \( P_\text{C} \) can be calculated by the formula [74,75]

\[
RT_{\nu \mu} \left[ C_{eq,\text{mat}} \ln \left( C_{eq,\text{mat}} / C_{eq,\text{mat}} \right) + \left( 1 - C_{eq,\text{mat}} \right) \ln \left( \left( 1 - C_{eq,\text{mat}} \right) / \left( 1 - C_{eq,\text{mat}} \right) \right) \right]
\]

Where \( R \) is the gas constant \( (8.31 \text{ J/mol.K}) \), \( V_{\nu \mu} \) is the molar volume of the precipitate \( (27.07 \text{ m}^3/\text{mol for Ni}_{x}\Al) \), \( C_{eq,\text{mat}} \) and \( C_{eq,\text{mat}} \) are the solute composition of supersaturated matrix (\( \sim 0.09 \)) and equilibrium precipitate (\( \sim 0.21 \)) and equilibrium matrix (\( \sim 0.04 \)). The \( P_\text{C} \) can be estimated to be \( 3.8 \times 10^7 \text{ J/m}^2 \) which is higher by order of magnitude than \( P_\text{D} \). Zener drag [76], \( P_\text{Z} \) is caused by the B2 ordered precipitates at the GBs and can be estimated by \( P_\text{Z} = 3 f \gamma_B / 2r \), where \( f = 0.08 \), and \( r = 160 \text{ nm} \) is the corresponding area fraction, and the average equivalent radius of B2 ordered precipitates. \( \gamma_B \) is the GB energy, assumed to be 0.625 J/m² [77]. The calculated Zener drag pressure is \( 0.46 \times 10^6 \text{ J/m}^2 \) which is of very low value as compared to the chemical driving force. This indicates the B2 precipitates are primarily responsible for enhancing the possible nucleation sites for recrystallization by PSN, and hence we obtained a fine recrystallized grain size in NCCA. The dominant factor for slowing down the GB migration velocity seems to be due to enhanced solute drag by the accumulation of solute at the boundary [78]. Hutchinson et al. [79] showed in Nb containing steel, solute drag by Nb is more dominant than the pinning by NbC precipitates in slowing down the ferrite GBs. In superalloys, Dahlen and Winberg [61] showed that the recrystallization kinetics becomes slower due to prior precipitates and their dissolution at the migrating GBs. They also observe nucleation of new grains on the recrystallization front once they cease to migrate. It was attributed to the increase in the drag force induced by the accumulation of solute at the migrating GBs. Porter and Ralph [67] mentioned that the rate at which the boundary moves depends on how fast it can dissolve the \( \gamma' \) precipitates and reprecipitates behind it. Hence, in the present case, Ni and Al have to rearrange themselves at the GB to form the ordered lamellae precipitates from a supersaturated solid solution.

Fig. 8. (a) A BSE image of NCCA alloy after HCA thermomechanical heat treatment from a non-recrystallized grain containing bright B2 precipitates. (b) Formation of new recrystallized grains in the vicinity of B2 precipitates (c) EBSD KAM map centered on a few B2 precipitates and (d) EBSD IPF map from the same region showing nucleation/growth and pinning of a new recrystallized grain by B2 precipitates.
This requires the diffusion of solutes along the migrating boundaries. As the GB moves, it expands, that leads to the increase in the diffusion path for the dissolving solutes to the lamella precipitates, which are only the sink available. This can lead to an increase in the solute concentration at the GBs and hence induces the solute drag. The solute drag pressure is calculated by $P_s = \frac{\alpha \gamma_{gb}}{L_s}$ [80]. Where $\alpha$ and $\beta$ are the solute drag parameters that directly proportional to temperature (T) and inversely proportional to the effective segregation energy ($E_s$) and effective solute diffusivity ($D_{gb}$) along the GBs. $c$ is the bulk solute concentration. The resultant solute drag force $P_s$ is inversely proportional to the $D_{gb}$ of the solute. APT analysis from moving GB shows pile up of Ni and Al in the front of the lamella precipitate [81]. Additionally, we also observe enrichment of Ni at the lamella precipitate/B2 interface. Hence, we propose that the solute drag is induced by the precipitate forming Ni and Al solutes which is most effective in reducing the velocity of the migrating GBs. A recent work on Ni-Co-Cr-Fe HEA, shows Ni as the slowest diffusing species among the other solutes [82].

4.3. Phase stability of strengthening L12 precipitates

Another important observation is that there is no evidence of L12 phase decomposition inside the recrystallization grains even after 500 h of annealing at 700 °C. However, in Fe containing HEAs, the L12 phase is unstable beyond 550 °C, and it decomposes to body-centered-cubic (bcc) ordered B2 phase inside the grains. Fe is well known for destabilizing L12 ordered structures in Ni-base alloys. Ma et al. [83] showed by experiments that by increasing Fe content (1 to 10 wt.%) in Ni-33Cr-10Al based alloy, the L12 structure phase starts disappearing, and other phases (bcc ($\beta$) and fcc ($\gamma$)) evolve in the microstructure. Thermodynamic Calculations (ThermoCal) supported the observations and revealed shrinking of $\gamma$' phase field and replacement by $\gamma + \beta$ phase-field as the Fe content increases in the alloy. This was attributed to the lowering of $\gamma$ and $\beta$ Gibbs free energies with the increase in Fe while Gibbs free energy of $\gamma'$ escalates that lowers the total Gibbs free energy by the formation of $\gamma + \beta$ phases. Similar destabilizing of L12 structure by Fe addition is reported in a non-equitatomic NiCoCrFeAl/Ti HEA/concentrated alloys promoting other undesirable phases [59,84]. It was also reported that doping of Fe into Ni$_2$Al L12 ordered lattice reduces the order-disorder transition temperature by ~ 180 °C, which directly relates to the lowering of their phase stability [85]. Hence, removal of Fe in the NiCoCrFeNiTi concentrated alloy led to an increase in the dissolution temperature by 90 °C and improved the high temperature coarsening resistance of L12 precipitates [84]. In the present MEA, since Fe is not present, the decomposition of L12 precipitates is expected to be prevented for a longer annealing time, as we also observed experimentally.

4.4. Deformation structure

We observe a higher strain/work hardening rate for NCCA. The tensile deformed/fractured microstructure reveals extensive twinning and the presence of SFs across the lamella structure. Even in NCC MEA, deformation twinning and SFs are seen in tensile deformed/fractured conditions and hence show a high degree of strain hardening. The tendency of twinning and formation of SFs is directly related to their low stacking fault energy (SFE $\sim$ 18 to 22 mJ/m$^2$) [15,86] that promotes easy dissociation of perfect dislocations into a/6<112> partial dislocations. The twinning and SFs act as strong barriers to the movement of dislocations and hence increases the strain hardening rates greater than several HEAs with higher SFEs. In the deformed/fractured NCCA alloy, we observe additional shearing of L12 ordered regions by the movement of dislocations and excessive local misorientations (Fig. 6) near the B2 precipitates. Hence, these combined factors induce a higher work hardening rate for NCCA alloy. cECCI images from the high temperature compressive deformed NCCA alloy reveal excessive sub-structure formation and dislocation entanglement around them, GBs and B2 precipitates indi-
cating their strong contribution in resisting deformation even at high temperatures.

5. Conclusions

In conclusion, NiCoCr MEA alloy offers enormous scope for developing structural alloys with promising mechanical properties under a wide temperature range, i.e., from cryogenic to high temperatures. The high sensitivity of the alloy towards alloying (Al) and thermo-mechanical processing (PR) resulted in a hierarchical microstructure consisting of recrystallized and non-recrystallized grains and ordered precipitates (L1₂ and B2). The sequence of microstructural development is illustrated schematically in Fig. 10. The composite microstructure displays a tensile 0.2% YS of ~1060 MPa, UTS of ~1335 MPa with ~25 % ductility at room temperature, and retains up to ~910 MPa at 670 °C. The microstructure is also stable at 700 °C up to 500 h. Deformed microstructures reveal extensive twinning and formation of stacking faults, shearing of L1₂ precipitates by dislocations, and strain accumulation at the GBs and B2 precipitates that resulted in higher strain hardening for NCCA alloy as compared to NCC alloy.

Future directions will be to do a detailed investigation of the deformation structure of non-recrystallized in the present MEA that promotes the nucleation of B2 and the deformation behavior of NCCA alloy at room and high temperatures. Since the dissolution temperature of strengthening L1₂ precipitates is 800 °C, a selection of further alloying such as Ta and Ti knew to stabilize the L1₂ ordered structure can improve the PR MEA microstructural stability at higher temperatures. Thus, it opens new possibilities for designing high-performance MEAs.

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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Supplementary materials

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