Contents lists available at ScienceDirect



Journal of Materials Science & Technology

journal homepage: www.elsevier.com/locate/jmst

Research Article

Manipulating grain boundary migration to fabricate integral core-shell structure with enhanced strain hardening in Ni-based high-entropy alloy



Hyojin Park^{a,b}, Qingfeng Wu^{b,c}, Yoon–Uk Heo^c, Sun Ig Hong^{c,d}, Rae Eon Kim^{b,c}, Do Won Lee^{a,b}, Soung Yeoul Ahn^{a,b}, Zhe Gao^e, Jae Heung Lee^{a,b}, Hyo Moon Joo^f, Jongun Moon^g, Young-Sang Na^h, Jae-il Jang^e, Hyoung Seop Kim^{a,b,c,i,j,*}

^a Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 37673, South Korea

^b Center for Heterogenic Metal Additive Manufacturing, Pohang University of Science and Technology (POSTECH), Pohang 37673, South Korea

^c Graduate Institute of Ferrous & Eco Materials Technology, Pohang University of Science and Technology (POSTECH), Pohang 37673, South Korea

^d Department of Materials Science and Engineering, Chungnam National University, Daejeon 34134, South Korea

^e Division of Materials Science and Engineering, Hanyang University, Seoul 04763, South Korea

^f Lightweight Materials Research Team, Advanced Vehicle Platform, Hyundai Motor Group, Uiwang 16082, South Korea

^g Division of Advanced Materials Engineering, Kongju National University, Cheonan 31080, South Korea

^h Korea Institute of Materials Science (KIMS), Changwon 51508, South Korea

ⁱ Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai 980-8577, Japan

^j Institute for Convergence Research and Education in Advanced Technology, Yonsei University, Seoul 03722, South Korea

ARTICLE INFO

Article history: Received 31 October 2024 Revised 31 March 2025 Accepted 19 April 2025 Available online 17 May 2025

Keywords: Core-shell structure Microstructure formation mechanism Grain boundary migration Strain hardening Precipitate

ABSTRACT

A core-shell microstructure represents an approach to achieve superior mechanical properties in alloys through its distinctive architecture, typically developed in powder metallurgy processing. In the present study, an integral core-shell structure has achieved in a cast Ni-based high entropy alloy through a straightforward thermo-mechanical processing (TMP) approach, including hot rolling and heat treatment. Inspired by the formation of a necklace structure during the hot deformation, we employed hot rolling to induce bulged grain boundaries in coarse grains. Subsequent heat treatment constrained the growth of these bulged regions through B2 precipitate formation, leading to the stabilization of the integral core-shell structure, where the deformed grains form the core, and the bulged grains form the shell. The significant synergistic hardening in the TMP-processed sample. The integrated TMP approach, combined with alloy design, enables the evolution of integral core-shell structures in cast high entropy alloys, significantly improving material properties without the complexities of powder metallurgy.

© 2025 Published by Elsevier Ltd on behalf of The editorial office of Journal of Materials Science & Technology.

1. Introduction

High-entropy alloys (HEAs) have emerged as a revolutionary class of materials, characterized by their unique composition, which includes more than four principal elements at high concentrations ranging from 5% to 35% [1,2]. This distinctive composition yields exceptional mechanical properties, with many studies demonstrating homogeneous microstructures reinforced by combined with precipitation strengthening [3,4], transformationinduced plasticity [5–7], and twinning-induced plasticity [8–10]. ious engineering applications. However, achieving an optimal balance between strength and ductility remains a critical challenge for HEA systems. To address this issue, the exploration of microstructural engineering has led to an increased interest in heterogeneous structures, including multimodal [11,12] and bimodal grain size distributions [13,14], eutectic lamellar structures [15,16], gradient structures [17,18] achieved through surface plastic deformation technique, and core-shell structures [19,20] fabricating via powder metallurgy. Compared to homogeneous structures, these heterogeneous structures lead to the accumulation of additional geometrically necessary dislocations (GNDs) at the interfaces of hard and soft domains, thus developing significant back stress. These enhancements improve the strength and capacity for strain hard-

These mechanisms position HEAs as promising candidates for var-

* Corresponding author. E-mail address: hskim@postech.ac.kr (H.S. Kim).

https://doi.org/10.1016/j.jmst.2025.04.017

1005-0302/© 2025 Published by Elsevier Ltd on behalf of The editorial office of Journal of Materials Science & Technology.

ening, a phenomenon known as hetero-deformation induced (HDI) strengthening [21–23].

Among these heterogeneous structures, core-shell structures are notable for their isotropic microstructure, where coarse core and fine shell grains are systematically organized into a threedimensional core-shell configuration, featuring a bimodal grain size distribution. This structural arrangement promotes uniform deformation across the material, contributing the stable deformation, in contrast to localized deformation in anisotropic heterogeneous materials [23]. A dense interface boundaries between coarse and fine grains inherent in the unique microstructure solve the problem of the strength-ductility trade-off because it exhibits superior ductility and enhanced HDI strengthening [22,23]. For instance, Li et al. [19] introduced a method to optimize the strength and ductility of the harmonic structure of an Fe₅₀Mn₃₀Co₁₀Cr₁₀ HEA prepared by powder metallurgy (PM) through controlled mechanical milling and sintering. Optimization of the shell region fraction to 70% was found to result in a twofold increase in yield strength while maintaining comparable ductility compared to the homogeneous structure [19].

Although core-shell structures yield excellent mechanical properties, their fabrication has generally been confined by the limits of the milling and sintering processes utilized in PM [19,20,24]. However, PM processing faces challenges in scaling up and subsequent manufacturing, necessitating the development of strategies to create harmonic structures in cast alloys, which are the most commonly employed in industrial applications. Although research in this area is limited, a few studies have been tried. For example, Du et al. [25] acquired a cast alloy (Co_{34,46}Cr_{32,12}Ni_{27,42}Al₃Ti₃) where precipitates at the grain boundaries, acting as a shell. However, the density of these precipitates led to localized stress concentrations, ultimately resulting in a strength-ductility trade-off.

Another approach involves dynamic recrystallization (DRX) to realize a necklace structure along grain boundaries during the early to middle stages of hot deformation, particularly in Fe/Ni-based alloys with low-to-medium stacking fault energy (SFE). This process involves strain-induced grain boundary migration (SIBM), where bulged grains form due to strain gradients between grains [26], resulting in a necklace structure. Continuous strain leads to growth accidents that inhibit the bulged grain growth, and sustain the cycle of new grain formation, consuming the entire original grains [27–29]. Although the necklace microstructure is typically transient during hot deformation and may have limited practical application in engineering materials due to challenges in scaling up, it inspires the development of a core-shell structure from the cast alloys. Controlling precipitation along the boundaries and stabilizing the SIBM in cast high-entropy alloys offers a promising strategies to form core-shell structure.

In this study, we demonstrate that an integral core-shell structure can be achieved in cast alloy through careful designs of the alloy composition and TMP. We utilized SIBM to form the bulged region as a shell and rely on the precipitate pinning effect to constrain the bulged region growth. The process of the unique coreshell structure was investigated for each TMP, and the deformation mechanism of the integral core-shell structure and the role of the precipitates are discussed in detail.

2. Experimental section

2.1. Design of alloy composition and thermo-mechanical process

The Ni-HEA, with a composition of Ni₃₅(FeCoCr)₅₃Al₇Ti₅ at.% and the TMP strategy were carefully designed. Computational thermodynamic calculations were employed to predict and determine the phase types and fractions that were compatible with those of our design strategy. The isothermal pseudo-ternary phase diagram at 900 °C and the equilibrium phase fraction, with temperature calculated by Thermo-Calc 3.0 using TCHEA database from the CMSE group [30], are shown in Fig. 1. In Ni-based HEAs strengthened by the L1₂ phase, a high fraction of L1₂ is preferred due to its potential to offer a compelling balance between strength and ductility. Conversely, brittle phases with a B2 structure are usually undesired owing to their tendency to form coarse precipitates at the grain boundaries, leading to premature fracture. However, in our alloy system, the B2 precipitate is designed to play a critical role in constraining the growth of bulged grains, thereby contributing to the stability of the core-shell structure and mechanical stability of the alloy. The selection of the alloy composition was guided by an isothermal pseudo-ternary diagram at 900 °C, as depicted in Fig. 1(a). An increase in the Al/Ti ratio above 1 induces not only a high volume fraction of L1₂ precipitates but also leads to the formation of B2 precipitates [31,32]. A high fraction of Ti leads to segregation at the grain boundaries during casting [33]; thus, a composition of 7 % Al and 5 % Ti was chosen to avoid grain boundary segregation. Fig. 1(b) presents a phase diagram of the Ni-HEA. For the TMP strategy, hot rolling was performed at 1200 °C, focusing on the single FCC phase region to achieve coarse grains and accumulate the requisite strain for SIBM. Then, it was followed by carefully controlled heat treatment at 900 °C, in which the formation of the highly brittle sigma phase was avoided, and a minor fraction of B2 and a high fraction of L1₂ precipitates were obtained. Finally, an additional aging process at 600 °C was conducted to enhance the mechanical performance through additional control of the microstructure, particularly focusing on the increase in the volume fraction of L1₂ precipitates and expansion of the bulged region, which are vital to understanding the microstructural evolution.



Fig. 1. (a) 900 °C isothermal pseudo ternary phase diagram of Al_x-Ti_y-(Ni_{39,77}(FeCoCr)_{60,23})_{100-x-y} and (b) phase diagram of Ni₃₅(FeCoCr)₅₃Al₇Ti₅ Ni-HEA.

2.2. Material preparation

A Ni₃₅(FeCoCr)₅₃Al₇Ti₅ (at%) Ni-based HEA was fabricated using vacuum induction melting (MC100V, Indutherm) with pure metal (> 99.99 wt%) under an argon atmosphere. A 50 mm × 35 mm × 7 mm rectangular ingot was subjected to a homogenization treatment at 1200 °C for 12 h. Subsequently, the ingot was hot-rolled to a final thickness of 1.5 mm from 7 mm, corresponding to a total thickness reduction of 78.5%, at a temperature of 1200 °C. The rolling process was designed such that each rolling pass resulted in a 15 % reduction in thickness. After every two passes, the alloy was reheated for 5 min at hot rolling temperature [7]. The hot-rolled material was annealed at 900 °C for 1 h, water-quenched, and followed by aging at 600 °C for 3 h, after which it was quenched in water. For ease of reference, the hot-rolled, annealed, and aged samples were denoted as "HR," "A900," and "A900+AG", respectively.

2.3. Mechanical testing

Flat dog bone-shaped samples were extracted from the hotrolled plate with dimensions of 5.0 mm in length, 2.5 mm in width, and 1.5 mm in thickness. Before tensile testing, the samples were mechanically polished using SiC abrasive paper up to 1200 grit to remove the oxidation layer. To ensure reproducibility, tensile tests were performed three times for each condition. Tensile tests were conducted using a universal testing machine (Instron M5582, Instron Corp., USA) at a constant strain rate of 10^{-3} s⁻¹, using the digital image correlation (DIC) (ARAMIS M12, GOM Optical Measuring Techniques, Germany) to measure precise strains. DIC imaging was employed to analyze the deformed microstructure at various local true strain levels (ε_{tr}) (see Supplementary Fig. S1 in the Supplementary materials). Although the coarse grain size of the samples is approximately 100 µm, the tensile gauge section contains over 18,000 grains (estimated using cube geometry) or approximately 35,000 grains (assuming spherical grains), ensuring that the mechanical properties measured are statistically representative of the material. The reliability of the tensile results, including yield strength (YS), ultimate tensile strength (UTS), and uniform elongation, is further supported by reference [34], confirming the negligible influence of sample size on these mechanical properties. The loading-unloading-reloading (LUR) tensile tests were conducted using the same equipment as the tensile tests to demonstrate the deformation mechanisms of the integral coreshell structure microstructure and quantify the HDI stress contribution. Microhardness measurement was performed on A900 samples using an HM-220B micro-Vickers hardness tester (Mitutoyo, Japan) on the electro-polished surface. A load of 10 gf was applied for a dwell time of 10 s. To ensure reliable data, at least ten measurements were taken for both the shell and core regions. Additionally, to minimize potential stress interference from adjacent indentations, indentations were spaced at a distance of at least three times the diagonal length.

2.4. Microstructural characterization

The microstructural characterization of the Ni–HEA was conducted in detail. Synchrotron X-ray diffraction (XRD) measurements were performed on the HR, A900, and A900+AG samples at the 8D beamline of the Pohang Accelerator Laboratory. The 8D beamline used an X-ray energy of 16.143 keV and a wavelength of 0.768 Å. The scan results for the three annealed samples were obtained in the 2θ range of 10° – 45° with steps of 0.01° and a holding time of 0.5 s per step. The convolutional multiple whole profiles (CMWP) method [35] was employed to evaluate the dislocation density in the HR, A900, and A900+AG samples through X-ray line profile analysis. This method involves the direct fitting of measured XRD patterns with theoretical functions that account for grain size, strain profiles, and background data. By processing the entire diffraction pattern, the CMWP method minimizes errors commonly associated with peak separation and instrumental calibration in traditional profile analysis. The instrumental broadening effect is nullified by the XRD analysis of a standard CeO₂ sample.

The precipitate microstructural characterization was achieved using field-emission scanning electron microscopy (FE-SEM, XL30S FEG, Philips and JSM-7100, Japan) with energy dispersive spectroscopy (EDS). Electron backscatter diffraction (EBSD) (JEOL ULTRA-55, Carl Zeiss, Germany) and FE-SEM were used to characterize the initial and deformed microstructures. The HR, A900, and A900+AG samples' microstructures, magnified microstructures, and deformed microstructures of the A900 sample were obtained through EBSD measurement using a step size of 0.4, 0.2, and 0.2 µm, respectively. The results were analyzed by orientation imaging microscopy (OIM) collection software (TSL OIM Analysis 7). The volume fraction and diameter of each type of precipitate were measured from SEM images using the ImageJ software (1.53e). For XRD and EBSD sample preparation, mechanical polishing was followed by electropolishing in a solution of 6% HClO₄ and 94% CH₃COOH. Furthermore, the precipitates and deformation behavior of the A900 sample were examined in detail via FE-transmission electron microscopy (TEM, JEM-2100F, JEOL Ltd., Japan). The preparation of the specimens for TEM analysis included mechanical thinning down to a thickness of approximately 70 µm, followed by further thinning using an electropolishing technique, employing a solution containing 10% HClO₄ and 90% CHCOOH at an applied voltage of 20 V at room temperature. Deformed A900 samples with local true strains of 2% and 12% were prepared through the focused ion beam lift-out procedure (SII SMI3050SE, SII Nanotechnology, Japan).

3. Results

3.1. Microstructure evolution through thermo-mechanical treatment

Fig. 2 displays the synchrotron XRD patterns of the Ni–HEA under three different conditions. For the HR sample, strong FCC peaks were prominent, as well as barely discernible B2 and L1₂ peaks, which are believed to have formed during air quenching after hot rolling. The A900 and A900+AG samples also exhibited pronounced FCC peaks, but weakly intense B2 and L1₂ peaks. A



Fig. 2. Synchrotron XRD patterns of the HR, A900, and A900+AG samples, indicating the presence of FCC with $L1_2$ and B2 structures. The XRD results are normalized with an FCC (111) plane peak set with a reference intensity 1.



Fig. 3. (a_1, a_2) Low magnification EBSD IPF map and phase maps, and (a_3, a_4) high magnification IPF and KAM map of the HR sample. Low magnification IPF, phase maps, and grain size distribution plots (b_1-b_3) for the A900 sample and (c_1-c_3) for the A900+AG sample.

magnified view of these samples reveals an increase in the peak intensities of B2 and $L1_2$ with subsequent heat treatments.

EBSD analysis was performed to elucidate the microstructural morphology resulting from TMP, Fig. 3 provides comprehensive maps of HR, A900, and A900+AG samples. The inverse pole figure (IPF) map of the HR sample (Fig. $3(a_1)$) confirms the presence of nonlinear annealing twins and serrated grain boundaries, reflecting the inhomogeneous deformation adjacent to the grain and twin boundaries during hot rolling. The gradient coloring in the grains is attributed to the local misorientation induced by the inhomogeneous deformation and the localized strain near the boundaries [36]. The phase map in Fig. $3(a_2)$ reveals the existence of an FCC single phase, which contrasts with the synchrotron XRD result, which suggests the presence of minor B2 and L1₂ phases; these phases were not detectable during the EBSD analysis because of the presence of sub-micron-sized B2 and L12 particles smaller than the EBSD step size (0.4 µm). The HR sample exhibits a typical homogeneous structure with an average grain size of 125.57 \pm 52.63 $\mu m.$ The kernel average misorientation (KAM) map (Supplementary Fig. S2) reveals a high dislocation density at the grain boundaries, supporting the presence of inhomogeneous deformation and the localized strain accumulation. Fig. $3(a_3 \text{ and } a_4)$ presents an enlarged view of the grain boundaries in the HR sample, revealing that the grain boundaries develop a serrated configuration and appear rugged, with approximately 1 µm protrusions, resembling the teeth of a gear wheel. The KAM map in Fig. $3(a_4)$ shows that the GNDs are locally accumulated adjacent to the grain boundaries, providing the driving force for recrystallization. Coarse grains with serrated grain boundaries are a typical feature of hotrolled structures [37]. Fig. 3(b and c) displays the distinctive microstructures of the A900 and A900+AG samples, respectively. Interestingly, both samples exhibit unique heterogeneous microstructures with expanded bulged regions that form thin shell areas, while the original coarse grains serve as the core, resulting in a distinct integral core-shell structure in Fig. $3(b_1 \text{ and } c_1)$. The

nearly full FCC phase structure with the minor body-centered cubic (BCC) phase (i.e., \sim 0.2% and 0.3% in the A900 and A900+AG samples, respectively) located at the grain boundaries is shown in Fig. 3 (b_2 and c_2). Thermodynamic calculations, synchrotron XRD results, and TEM analyses confirm that the BCC phase consists of B2 precipitates. Fig. $3(b_3 \text{ and } c_3)$ indicates that the grain size distributions of these samples show a characteristic bimodal distribution. Both samples maintain coarse regions with grain sizes of ${\sim}100~\mu m$. In the A900 sample, the shell region has an average size of 10.27 \pm 6.90 µm, with an average thickness of 7.73 \pm 3.10 µm accounting for 9.20% of the volume fraction. In the A900+AG sample, the volume fraction of the shell wall region nearly doubles to 17.31%, with the average size of 12.67 \pm 8.42 μm and thickness of 13.11 \pm 5.17 $\mu m.$ During aging, the area fraction of the shell wall regions expands; however, their sizes remain relatively constant, effectively maintaining the integral core-shell structure. These findings suggest that the core-shell structure may be further manipulated and modified through subsequent heat treatments.

The traditional core-shell structure consists of multiple coarse grains clustering together to form the core, with the coarse grain surrounded by a layer of fine grains formed at its grain boundaries, exhibiting a bimodal grain size distribution [19,23]. As shown in the magnified A900 sample (Fig. 4), a coarse grain is enveloped by the shell region. More precisely, a single coarse grain consists of a central core region and a peripheral shell region, forming an integral core-shell structure. During heat treatment, the preexisting bulged regions formed during hot rolling [38] expanded by intruding into adjacent grains. As these areas expand and overlap, their growth is controlled by the precipitation, forming a symmetric shell region along the prior grain boundary, aligning with the orientation of the opposing coarse grains as discussed in Section 4.1. In addition, the recrystallized grains with random orientations are formed occasionally at grain boundaries with sufficiently high dislocation density. A comprehensive exploration of the formation mechanism, deformation behavior, and contributions



Fig. 4. Magnified A900 image showing the integral core-shell structure.

to strain hardening and YS of this unique core-shell structure will be further discussed in Sections 4.1, 4.3, 4.4, and 4.5.

Fig. 5(a and b) presents SEM and TEM results of the HR samples, respectively. The HR sample exhibits grain sizes exceeding 100 µm, consistent with the EBSD results (Fig. 3(a)). Upon magnification in Fig. 5(a1), the interior grains reveal a highly deformed structure with planar slip bands. Nano-sized L1₂ precipitates, approximately 2 nm in size, are observed in the dark-field image of Fig. $5(b_1)$, although they exist at a volume fraction of less than 1%. A bright-field scanning transmission electron microscopy (STEM) image in Fig. 5(b₂) reveals that grain boundary bulging occurred between two adjacent grains during hot rolling, with the bulged region extending into the opposite grain. These regions are symmetrically distributed along the prior grain boundary, as indicated by the white dashed line. The dark-field image in Fig. $5(b_3)$, taken from the highlighted area shown in Fig. $5(b_2)$, confirms that region A and region a share the same SAED pattern (Fig. 5(b₂)), verifying that they belong to the same grain. This bulging process leads to the formation of region a. The bulged region is composed of cellular-shaped L1₂ precipitates, as shown in Supplementary Fig. S3. In contrast, the as-cast sample (see Supplementary Fig. S4) displays coarse grains exceeding 1 mm in size and 30 nm spherical precipitates dispersed within the matrix. This indicates that the combination of high strain and elevated temperature during hot rolling led to the dissolution of existing grains and precipitates.

Fig. 6 presents the BSE and SE images of the A900 and A900+AG samples, demonstrating the varied morphologies of the precipitates in the shell regions. Three distinct types of precipitates, classified based on their morphology and location, can be identified: (1) Coarse, dark-colored B2 precipitates, measuring approximately 200–500 nm in size, observed at the bulged grain boundaries in Fig. $6(a_1 \text{ and } b_1)$. (2) Cellular-shaped L1₂ precipitates, measuring approximately 100–200 nm, formed along the bulged grain boundaries, as shown in Fig. $6(a_2 \text{ and } b_2)$. Both B2 and cellular-shaped L1₂ precipitates are concentrated in the bulged region, whereas (3) spherical nano-sized L1₂ precipitates, measuring 20–30 nm in size, are uniformly distributed throughout the whole matrix, as demonstrated in Fig. $6(b_3 \text{ and } c_3)$.

The growth of all three types of precipitates was pronounced in the A900+AG sample. Notably, a slightly increased fraction of B2 precipitates is observed in Fig. $6(b_1)$. B2 precipitates nucleate preferentially at grain boundaries, contributing to less than 1% of the total volume, as evidenced by the EBSD phase maps in Fig. $3(b_2$ and $c_2)$. Cellular L1₂ precipitation, driven by a discontinuous precipitation mechanism, originates from the solute concentration gradient across the grain boundary [37,39]. These discontinuous L1₂ precipitates preferentially form perpendicular to bulged grain boundaries, whereas spherical L1₂ precipitates, which form through a continuous precipitation mechanism, remain uniformly distributed throughout the matrix [40].

Discontinuous L1₂ precipitates exhibit more significant growth in the A900+AG sample than in the A900 sample. Regarding the continuous L1₂ precipitates, the initial heat treatment at 900 °C promoted bulk diffusion and the formation of relatively large continuous L1₂ precipitates (diameter: 26.76 ± 8.81 nm, volume fraction: 6.5%) in the A900 sample. The aging process, which occurred at the reduced temperature of 600 °C, ensured that the matrix remained supersaturated with solute and thus continued to promote the precipitation of continuous L1₂. However, the growth of the precipitate was retarded at a lower temperature, resulting in an average diameter of 30.26 ± 8.20 nm and a significant increase in the volume fraction to 20.0%.

TEM analysis confirmed the structure and chemical composition of these three precipitates, as presented in Fig. 7. The STEM-High-angle annular dark-field (HAADF) imaging in Fig. 7(a) shows all three distinct types of precipitates. The selected area electron diffraction (SAED) pattern in Fig. 7(a₁) for the coarse precipitate



Fig. 5. SEM and TEM analyses of the HR sample: SEM image at various magnifications $(a_1) 200 \times$, $(a_2) 1500 \times$. (b_1) Dark-field TEM image in the matrix showing nano-sized L1₂ precipitates. (b_2) Bright-field STEM image at the grain boundary showing bulged grain boundaries. (b_3) Dark-field image showing the local area of (b_2) , and (b_4) SAED pattern of (b_3) . Dark-field images were obtained from the red circle spot in the SEAD pattern.



Fig. 6. SEM microstructures of (a) A900 and (b) A900+AG at different magnifications: (a_1) and (b_1) 4500×, illustrating the triple junction; (a_2) and (b_2) 10000×, recrystallized fine grains; and (a_3) and (b_3) 35000×, revealing grain interiors. Images (a_3) and (a_3) are SE images.



Fig. 7. TEM analysis of the A900 sample microstructure: (a_1) HAADF image and SAED pattern of the B2 structure, (a_2) corresponding EDS maps, (b_1) dark-field image and SAED pattern of cellular-shaped discontinuous L1₂, (b_2) corresponding EDS maps, and (c_1) dark-field image and SAED pattern of spherical-shaped continuous L1₂ and (c_2) corresponding EDS maps. All ordered spots of the precipitates are indicated by dashed-line circles. Dark-field images were obtained from the spot marked with a red circle on each SAED pattern.

 Table 1

 Tensile properties of the Ni-HEA under three conditions.

Conditions	Yield strength (MPa)	Ultimate tensile strength (MPa)	Uniform elongation (%)	Total elongation (%)
HR A900 A900+AG	$\begin{array}{l} 738\pm8\\ 860\pm4\\ 1029\pm8 \end{array}$	947 ± 8 1185 ± 1 1271 ± 13	$\begin{array}{l} 31.8\pm1.3\\ 24.8\pm0.6\\ 23.2\pm0.4 \end{array}$	$\begin{array}{l} 46.5 \pm 4.6 \\ 32.0 \pm 1.4 \\ 31.1 \pm 1.3 \end{array}$

reveals a B2 structure. STEM-EDS maps (Fig. $7(a_2)$) show that the Ni(Al, Ti) B2 precipitates are enriched in Ni, Al, and Ti but depleted in Cr and Fe. In contrast, the dark-field images and SAED patterns in Fig. 7(b and c) reveal the discontinuous and continuous Ni₃(Al, Ti) L1₂ precipitates, respectively. Compared to B2 phase, L1₂ precipitates have higher Ni concentrations, with slight Al and Ti segregation. Their compositional differences arise from distinct formation mechanisms, as summarized in Supplementary Table S1.

3.2. Tensile properties

The representative engineering stress-strain curves for the HR, A900, and A900+AG samples are depicted in Fig. 8(a) and summarized in Table 1. The HR sample had a YS of 738 MPa, a UTS of 947 MPa, and a total elongation of 46.5%. Subsequent annealing of the A900 sample resulted in an enhanced YS of 860 MPa and UTS of 1185 MPa, and the total elongation reduced to 32.0%. Interestingly, upon further aging, the YS and UTS of the A900+AG sample increased to 1029 and 1271 MPa, respectively, maintaining a ductility similar to that of the A900 sample at 31.1%. This strength enhancement was achieved without compromising the ductility of A900 and A900+AG samples.

The strain hardening rates as a function of the true strain for the three samples are presented in Fig. 8(b). The HR sample exhibited a steadily decreasing strain hardening rate and deformation behavior that is characteristic of coarse-grained structures dominated by dislocation activity [41]. In contrast, the A900 sample exhibited a notable uprising in strain hardening rate, peaking at an impressive 3.4 GPa at a true strain of 12%, which is twice that of the HR sample at the same strain level. For the A900+AG sample, the initial drop in strain hardening rate was more pronounced compared to the A900 sample. However, it subsequently increased, ultimately reaching a peak strain hardening rate of 3.2 GPa, similar to that of the A900 sample. Despite the larger initial drop, the A900+AG sample exhibited a more significant SHR increment, demonstrating superior strain hardening capability. The notable differences in the strain hardening behavior between the heat-treated A900, A900+AG, and HR samples suggest the effects of thermal processing-induced microstructural modification on the predominant deformation and strain hardening mechanisms.

4. Discussion

4.1. Integral core-shell structure formation and stability mechanism

The integral core-shell structure originates from localized bulging at the grain boundaries during hot rolling. Subsequent heat treatment leads to the simultaneous formation of both core and shell regions within a single grain. To elucidate the underlying mechanism, we characterize the microstructural evolution of the hot-rolled and heat-treated samples.

Hot rolling, which involves thermal and strain energy applications, induces dynamic recrystallization and/or recovery. In Ni-HEAs with low to medium SFEs, dislocation climb and cross-slip are suppressed, which limits dynamic recovery while favoring dynamic recrystallization [29,42-45]. It was suggested that the formation of equilibrium grain boundaries is more difficult during hot rolling due to the lower driving force for forming a low-energy boundary structure since the strain energy accumulated during hot rolling is lower than that after cold rolling [38]. Dislocations with the same signs are expected to be pushed against the grain boundary due to the localized strain during hot rolling, and extra dislocations that sink into the existing boundary may increase the local grain boundary energy, producing deformation-distorted structures including grain boundary bulges and steps. The presence of grain boundary bulging may suggest that they are nonequilibrium boundaries with the extra dislocations of the same character impinged on the boundary during hot rolling [38,46] and/or the boundaries with the stored energy differentials between adjacent grains [26]. This bulge-forming process ceases when energy equilibrium is achieved, balancing the increased surface energy of the bulged boundary with the reduced strain energy of the grains [26,27]. As shown in Fig. 5(b), the formation of bulged regions is accompanied by the growth of discontinuous L1₂ precipitates. Additional dislocations are generated in the bulged grain-boundary regions (see Fig. $3(b_2)$) to accommodate the strain mismatch caused by deformation incompatibility in the locally heterogeneous region [47]. This localized deformation can drive the growth of bulged regions during further heat treatment.

To analyze the microstructural evolution during the heat treatment, the sample is subjected to a 10-min heat treatment at



Fig. 8. (a) Representative tensile engineering stress-strain curves of Ni-HEA samples. (b) True strain-stress curves and corresponding strain hardening curves of the Ni-HEA samples.



Fig. 9. High magnification EBSD analysis of the HR, 10-min heat treatment at 900 °C, A900, and A900+AG samples. Each set includes IPF, phase, and KAM maps: (a_1, a_2, a_3) for the 10-min heat treatment at 900 °C sample, $(b_1, b_2, and b_3)$ for the A900 sample, and $(c_1, c_2, and c_3)$ for the A900+AG sample.

900 °C and subsequently analyzed (Fig. 9(a)). The pre-existing bulged grain boundaries, which form during hot rolling, expand by approximately 5 µm in thickness during annealing (the dashed line in Fig. $9(a_1)$). Two distinct characteristics, indicated by the IPF map and SEM image in Fig. $9(a_1)$ and Supplementary Fig. S5(a), are observed within the bulged regions under annealing. Region A shows the growth of discontinuous L1₂ precipitates at the grain boundaries, leading to further migration and formation of expanded bulged regions. Conversely, region B shows constrained expansion owing to the presence of B2 precipitates (shown as dark particles in Supplementary Fig. S5(a)). The B2 precipitates, rich in Ni-Ti-Al, impose a grain boundary pinning effect, effectively restricting the expansion of the bulged regions. This phenomenon also causes local depletion of Ni, Ti, and Al within the matrix, thus reducing the SFE formation of stacking faults-precursor structures that facilitate annealing twin nucleation [48]. During the bulging process, variations in stored energy and dislocation rearrangement lead to localized misorientation accumulation, resulting in regions with high KAM values, as shown in Fig. $9(a_3-c_3)$ [47].

In the A900 sample in Fig. 9(b), bulged grains grow symmetrically as they expand from both sides of the grain boundary (indicated by arrows in Fig. 9(b₁)). This growth leads to the formation of a symmetric shell structure as the bulged region extends into the neighboring grains. The B2 precipitates at the grain boundary grow to a detectable size (confirmed by the phase map in Fig. 9(b₁)), effectively inhibiting the expansion of the bulged regions. Han et al. [49] performed cellular automata modeling to simulate static recrystallization following dynamic recrystallization-assisted bulged grain formation. Similar to our findings, their results demonstrated that pre-existing bulged grains could expand, eventually consuming the original grains and reverting to a homogeneous structure during static heat treatment. In contrast, our study achieves the formation of an integral core-shell

structure through precisely engineered alloy design and meticulous heat treatment temperature control.

In the A900+AG sample aged at 600 °C, the shell region expanded to 17.3%, nearly twice the fraction observed in the A900 sample (9.2%). This expansion is attributed to the suppression of B2 precipitation and growth at lower temperatures, which instead promotes the formation of discontinuous L1₂ precipitates. While B2 precipitates locally at pin grain boundaries during annealing, the surrounding segments remain free to migrate, producing the characteristic bowed (convex) boundary shape during aging. Specifically, migrating grain boundaries associated with discontinuous L1₂ precipitates exhibit a more convex morphology, as shown in Fig. 9(c) and Supplementary Fig. S5(b) and S5(b₁).

The convex morphology of the migrating grain boundaries enhances atomic rearrangement and strain relaxation, further increasing the probability of twin boundary formation [48], as confirmed by the increased twin boundary density in the expanded shell region (Fig. $9(a_2-c_2)$). At lower temperatures, the pronounced formation and growth of discontinuous L1₂ precipitates alongside grain boundary migration further contribute to shell region expansion by exerting a dragging effect on pinned boundaries, promoting additional growth.

Supplementary Fig. S6 presents a low-magnification IPF map and corresponding grain size distributions for the samples annealed at 900 °C for 10 min and 3 h. The bulged regions measure approximately $8.37 \pm 5.90 \ \mu\text{m}$ and $11.36 \pm 8.83 \ \mu\text{m}$ in diameter, while their fractions remain at 6.8% and 11.4%, respectively, indicating that the overall structure remains highly stable at this temperature. The rapid formation and growth of B2 precipitates strongly pin the grain boundaries, markedly restricting shell region expansion. In contrast, lower-temperature aging promotes the growth of discontinuous L1₂ precipitates accompanied by grain boundary migration, instead of B2 precipitation, ultimately yielding



Fig. 10. (a) STEM image of the deformed A900 microstructure at local true strain (ε_{tr}) 2%, and (b) and (c) high-resolution TEM image of the deformed A900 microstructure at ε_{tr} 12% (stacking faults indicated by light orange dashed lines and Lomer–Cottrell lock indicated by the orange circle).

a shell region nearly twice as large as that of the A900 sample. The combined effect of bulging and controlled precipitation results in an integral core-shell structure. B2 and discontinuous $L1_2$ precipitates, concentrated along the bulged grain boundaries, effectively distinguish the shell and core regions. This unique integral core-shell structure has been successfully developed by controlling the alloy composition and TMP to realize the desired microstructural evolution.

4.2. Interaction between precipitates and dislocations

In addition to causing grain-scale heterogeneous deformation, the precipitates in the A900 and A900+AG samples influence the deformation behavior. We conducted TEM analyses of the deformed microstructure of the A900 sample to investigate the nanoscale interactions between L12 precipitates and dislocations, as well as the overall deformation behavior. The STEM images obtained at 2% local true strain (ε_{tr}) in Fig. 10(a) show numerous dislocation pairs, which reflect the splitting of a perfect dislocation into two partial dislocations accompanied by the formation of an anti-phase boundary (APB). These pairs (highlighted by orange arrows) suggest that a shearing mechanism is active within the superlattice structure of the spherical $L1_2$ precipitates [50–52], especially when the diameter of the precipitate is similar to or exceeds the spacing between the dislocation pairs [50]. The highresolution TEM images at 12% ε_{tr} are shown in Fig. 10(b and c), showing a stacking fault extending along the {111} plane from the FCC matrix to the L1₂ precipitate. This observation indicates that dislocations penetrate the L12 precipitates, demonstrating a shearing mechanism that aligns with the deformation behavior observed at 2% $\varepsilon_{\rm tr}$. The shearing mechanism of L1₂ precipitates is known to enhance ductility and strain hardening by allowing dislocations to traverse the precipitates without creating critical stress concentrations [53,54]. In contrast, B2 precipitates at the shell-region grain boundaries (200-500 nm) act as dislocation accumulation sites, creating local stress concentrations that can potentially facilitate crack initiation [55]. Fig. 10(c) illustrates the formation of a Lomer-Cottrell lock at the intersection of two stacking faults; it effectively pins dislocations from several directions, thereby hindering their movement and leading to a significant dislocation pile-up. Such dislocation activity constitutes a typical deformation behavior in Ni-based HEAs and superalloys [56,57]. TEM and EBSD analyses reveal no deformation twin in the present alloy.

4.3. Origin of the improved yield strength

Compared to the YS of the HR sample (~738 MPa), the A900 sample exhibits an increased YS (~860 MPa). Subsequent aging at

600 °C (A900+AG sample) leads to an additional enhancement, resulting in a YS of approximately 1029 MPa. The improvement in YS can be attributed to microstructural evolution (i.e., grain size distribution, dislocation density, and precipitates). To quantify the synergistic effect of these factors, we quantify the grain boundary strengthening, Taylor strengthening, and precipitation strengthening of each sample.

Eq. (1) for grain boundary strengthening [58,59] is as follows:

$$\sigma_{\rm gb} = K_{\rm y} d^{-1/2} \tag{1}$$

where K_y is the Hall–Petch strengthening coefficient, here assumed to be 516 MPa $\mu m^{-1/2}$ for the FCC-structured Ni_{32.8}Fe_{21.9}Co_{21.9} Cr_{10.9}Al_{7.5}Ti_{5.0}, as reported by Fan et al. [60], and *d* is the average grain size. The HR sample exhibits a uniform grain size distribution, averaging 125 μm , resulting in a grain size contribution of approximately 46.15 MPa.

In the A900 and A900+AG samples, grain growth was observed. However, instead of forming low-energy hexagonal shapes, the grains have grown into irregular shapes due to the localized expansion of the bulged regions from the original grains. It is assumed that the high density of B2 precipitates and grain/twin boundaries within the bulged regions could effectively impede dislocation movement between the bulged and original regions. Additionally, B2 precipitates nucleated at grain boundaries are expected to exert a pinning effect, restricting the growth of the shell region and maintaining a finer shell grain size. Therefore, by assuming a bimodal grain structure, we calculated the maximum strengthening contribution that our integral core-shell structure could achieve. The bimodal grain size distribution model is utilized as follows (Eq. (2)).

$$\sigma_{\rm gb} = K_{\rm y} \cdot \left(d_{\rm s}^{-1/2} \cdot V_{\rm s} + d_{\rm c}^{-1/2} \cdot V_{\rm c} \right) \tag{2}$$

where d_s represents the average grain size of the shell region (bulged region), and d_c is the average grain size of the core region (original region). V_s and V_c are the volume fraction of the shell and core regions, respectively. The core region averages 100 µm, while the shell regions had grain sizes of 10.27 µm (9.20% volume fraction) for A900 sample and 12.67 µm (17.31%) for A900+AG sample. The contribution of YS from grain boundary strengthening is calculated to be 63.60 MPa for the A900 sample and 69.57 MPa for the A900+AG sample, indicating a slight enhancement due to the presence of the shell region. Although the initial microstructure features coarse grains over 100 µm, with the shell region grain size around 10 µm, the relatively low volume fraction of the shell region limits the YS enhancement effect from the bimodal grain size distribution, making it not significant.



Fig. 11. (a) LUR true plastic stress-strain curve of the A900 and A900+AG samples, (b) evolution of σ_{HDI} and σ_{eff} , measured from the hysteresis loops in (a), and (c) back stress contribution.

The Taylor strengthening mechanism is described by the following Eq. (3) [61]:

$$\Delta \sigma_{\rm dis} = M \alpha G b \rho^{1/2} \tag{3}$$

where *M* is the Taylor factor (3.06 for FCC materials), α is a constant related to material deformation, G is the shear modulus, *b* is the Burgers vector (= 0.254 nm, measured from the synchrotron XRD results), and ρ is the dislocation density (6.51×10^{14} m⁻² for the HR sample, 4.32×10^{14} m⁻² for the A900 sample and 3.96×10^{14} m⁻² for the A900+AG sample). The dislocation density is derived from the synchrotron XRD results using the CMWP method. The Taylor strengthening contributions are 319.35, 260.20, and 249.11 MPa for the HR, A900, and A900+AG samples, respectively. The annealing and aging processes do not significantly affect dislocation density.

The YS differences between the HR, A900, and A900+AG samples are primarily attributed to variations in the precipitation strengthening. Particularly, the strengthening is significantly influenced by the volume fraction of spherical L1₂ precipitates. Since the B2 precipitates account for less than 1% of the total volume, their direct contribution to precipitation strengthening is negligible. Synchrotron XRD in Fig. 2 and TEM in Fig. 5(b₁) analyses also reveal a minimal presence of these precipitates in the HR sample, indicating negligible precipitation strengthening. In contrast, the A900 and A900+AG samples exhibit enhanced precipitation, with spherical L1₂ precipitates measuring approximately 30 nm at volume fractions of 6.5% and 20.0%, respectively. In L12strengthened Ni-based HEAs, ordering strengthening is the predominant mechanism when the size of the precipitates is below 35 nm [62,63]. Details on the calculation of the critical radius for determining the dominant precipitation strengthening mechanism are provided in Supplementary Fig. S7 and the Supplementary Materials. This process involves the formation of APBs, which critically affect strengthening as dislocations shear the precipitates, and is described quantitatively by the following Eq. (4) [64]:

$$\Delta \sigma_{\rm ppt} = M \cdot 0.81 \left(\frac{\gamma_{\rm APB}}{2b}\right) \left(\frac{3\pi f}{8}\right)^{1/2} \tag{4}$$

where γ_{APB} is the APB free energy of the precipitate (= 0.12 J/m² from Ni-based superalloy [65]), and *f* is the volume fraction of the L1₂ precipitate. The impact of this shearing mechanism is quantitatively significant, contributing 161.83 and 283.64 MPa to the YS of the A900 and A900+AG samples, respectively.

Based on the grain boundary strengthening, Taylor strengthening, and precipitation strengthening theories, the YS contributions for the HR, A900, and A900+AG samples are 361.6, 479.1, and 595.3 MPa, respectively. The theoretical differences in YS between the HR and A900 samples and between the HR and A900+AG samples are calculated to be 117.5 and 233.6 MPa, respectively. These values are close to the respective experimental values of 122 and 291 MPa, illustrating the successful quantification of the YS enhancing factors that arise during microstructural evolution. The primary contribution to the observed differences in YS among these samples primarily stems from the precipitates, confirming their significant role in mechanical strengthening.

4.4. Hetero deformation-induced strengthening of the integral core-shell structure

The integral core-shell structure of the A900 and A900+AG samples exhibits excellent strain hardening behavior due to a heterogeneous deformation mechanism, primarily driven by HDI strengthening. In this mechanism, the pile-up of GNDs at interfaces between regions contributes to strain hardening. To quantify this effect, load-unload-reload (LUR) tests were conducted to calculate the HDI stress ($\sigma_{\rm HDI}$) and effective stress ($\sigma_{\rm eff}$). Fig. 11 presents the LUR test results for both the A900 and A900+AG samples, showing increasingly pronounced hysteresis loops with strain. The $\sigma_{\rm HDI}$ and $\sigma_{\rm eff}$ values are derived using Eq. (5) [66],

$$\sigma_{\text{HDI}} = \frac{\sigma_{\text{r}} + \sigma_{\text{u}}}{2} \tag{5}$$

where σ_r and σ_u represent the yield stresses during reloading and unloading, respectively; $\sigma_{\rm eff}$ is determined by subtracting σ_{HDI} from the flow stress (σ_{f}) for each applied strain [66,67]. At 16% true strain, the A900 sample exhibits a $\sigma_{\rm HDI}$ of 833 MPa, more than twice the value of $\sigma_{\rm eff}$ with a $\sigma_{\rm HDI}/\sigma_{\rm f}$ ratio of 0.62– substantially higher than values reported in previous studies on other heterostructure materials [68–72]. This demonstrates the enhanced back stress strengthening effect of the core-shell structure. In the A900+AG sample, $\sigma_{\rm HDI}$ exceeds 1 GPa, with a $\sigma_{\rm HDI}/\sigma_{\rm f}$ ratio averaging \sim 0.67. This suggests that the A900+AG sample exhibits even greater HDI strengthening, attributed to its nearly doubled shell fraction due to its increased thickness compared to the A900 sample, while maintaining a similar shell diameter. The increased shell fraction enhances dislocation accumulation in the shell and pile-up at the boundary, reinforcing strain partitioning and improving strain hardening.

4.5. Strain hardening behavior of the integral core-shell structure

Heterogeneous deformation behavior is typically associated with dislocation pile-up at interfaces due to differences in dislocation mobility and microstructural constraints [73]. In this alloy, the matrices of the core and shell regions exhibit a hardness difference (Supplementary Fig. S9), which becomes more pronounced during deformation. The coarse-grained core region, containing shearable continuous L1₂ precipitates, provides minimal resistance to dislocation motion, allowing dislocations to move easily. On the other hand, the shell region—strengthened by non-shearable B2 and discontinuous L1₂ precipitates, as well as abundant grain, phase, and twin boundaries—acts as a strong obstacle to dislocation movement. These features lead to an increase in both geometrically necessary dislocations (GNDs) as well as statistically accumulated



Fig. 12. ECCI and EBSD analyses of the deformed microstructure of the A900 sample at various ε_{tr} . Each set includes ECCI images of (a_1-d_1) core and (a_2-d_2) shell and interface, and (a_3-d_3) KAM and (a_4-d_4) phase maps at triple junction: (a) at 5% ε_{tr} , (b) at 10% ε_{tr} , (c) at 15% ε_{tr} , and (d) at 20% ε_{tr} .

dislocations (SSDs), promoting HDI strengthening and strain partitioning. Additionally, B2 precipitates play a dual role: (1) stabilizing the core-shell structure through suppression pinning of bulged grain growth and boundaries, and (2) acting as strong dislocation barriers during deformation, contributing to back stress hardening and overall mechanical performance. Moreover, the irregular morphology and associated internal stress in the shell promote GND accumulation [47], further enhancing HDI strengthening by intensifying dislocation interactions at the core-shell interface.

ECCI analysis was performed to examine the deformation microstructure of the A900 sample at true strain $\varepsilon_{\rm tr}$ levels of 5%, 10%, 15%, and 20%, focusing on both the core and the core-shell interface regions. Fig. 12 (a_1-d_1) shows that planar slip lines progressively develop in the core region; however, their contribution to strain hardening remains limited in the absence of strong barriers to dislocation motion [74,75]. At 5% ε_{tr} (Fig. 12(a₂)), planar primary slip bands are visible across the grain interiors, except in regions near grain boundaries. On the other hand, at 10% ε_{tr} (Fig. 12(b₂)), secondary slip lines as well as the planar primary slip lines are observed, even in grain interiors far from grain boundaries. In lowto-medium SFE FCC alloys such as Ni-Fe-Co-Cr alloys, primary slip dominates at low strains due to restricted cross-slip, leading to thickening of planar slip bands and an initially low strain hardening rate [74]. This effect is particularly pronounced in large-grained materials [75]. In planar slip allovs, secondary slip typically activates only after primary slip fills the grain interior and finds no easier path, developing stage II hardening after the initial stage of low hardening rate [74,75]. The HR sample, composed of coarse grains, exhibits a similar planar slip-dominant deformation mode (Fig. 8(b)), which explains its relatively low strain hardening capacity. Within the core region, slip remains primarily confined to well-defined slip planes, allowing dislocations to move relatively easily.

However, Fig. $12(a_2-d_2)$ shows pronounced slip activation near the core-shell interface, where secondary slip planes emerge to accommodate slip inhomogeneity adjacent to the shell-region boundaries, leading to the formation of significant geometrically necessary dislocations and dislocation pile-ups. In contrast, the shell region exhibits significantly reduced dislocation activity at low strains (Fig. $12(a_2-b_2)$), as strong barriers such as B2 and discontinuous L1₂ precipitates, along with grain and twin boundaries, restrict dislocation motion.

To further validate the strain partitioning observed in the ECCI, EBSD was conducted at $\varepsilon_{\rm tr}$ of 5%, 10%, 15%, and 20% of the A900 sample (Fig. 12 (c, d)). The KAM value, initially 0.485° ± 0.549° at 5% $\varepsilon_{\rm tr}$, increases to 0.967° ± 0.7113° at 20% $\varepsilon_{\rm tr}$, providing evidence of continuous GND accumulation with increasing strain. The relationship between KAM and GND density is given by [76],

$$\rho_{\rm GND} = \frac{2\theta}{ub} \tag{6}$$

where *u* is the step size (150 nm), *b* is the magnitude of the Burgers vector, and θ is the average local misorientation angle measured in KAM maps.

At 5% ε_{tr} in Fig. 12(c₃), the KAM value remains largely unchanged, particularly in the region near B2 precipitates and grain/twin boundaries, where KAM values show only a slight increase. As deformation progresses, these regions exhibit a significant and continuous increase in KAM values (Fig. 12(c₃, d₃)), confirming their role as major dislocation barriers that promote dislocation storage associated with GND pile-ups and strain partitioning. The lattice mismatch between cellular-shaped discontinuous L1₂ precipitates and the FCC matrix increases local strain energy,

which enhances dislocation interaction and promotes GND accumulation in the shell [77]. The increasing KAM values at the coreshell interface further indicate that GND accumulation accommodates strain incompatibility between the core and shell regions. Notably, while ECCI observations confirm active slip in the core, they also suggest that planar slip in the core is primarily accommodated through well-defined planar slip bands, allowing dislocations to move with minimal lattice rotation and misorientation accumulation [78].

The increased strain hardening in A900+AG sample is primarily attributed to its enhanced contribution of back stress hardening, as shown in Fig. 11. The increased shell fraction in this sample is linked to the greater density of grain boundaries and B2 precipitates, which enhance dislocation pile-up and GND accumulation. Additionally, irregular grain boundaries contribute to the generation and accumulation of GNDs, leading to a pronounced development of greater back stress. These findings confirm that the increased shell fraction, stabilized by abundant irregular grain boundaries and precipitates, plays a dominant role in improving strain hardening within the integral core–shell structure.

The initial strain hardening rate in the A900 and A900+AG samples is primarily influenced by the dominance of planar slip at low strains, a characteristic behavior of low-to-medium SFE alloys where cross-slip is limited [74], particularly dominated in largegrained materials [75]. In the A900+AG sample, this effect is further intensified by the depletion of Ni, Ti, and Al due to the additional B2 and L1₂ phases precipitation during aging. This compositional change further lowers the SFE of the matrix, promoting planar slip while restricting secondary slip activation at low strains [79-81]. However, once the grain interior becomes saturated with primary slip dislocations, the strain hardening rate increases significantly due to the activation of secondary slip, facilitated by the increased flow stress and the stress concentration induced by grain and/or shell boundaries [74,75]. Previous studies have demonstrated that reducing microstructural length scales and activating secondary slip systems significantly enhance strain hardening [74,75].

In the early stages of deformation, dislocation pile-up at B2 precipitates and grain boundaries induce back stress hardening, while GND accumulation at the core-shell interface compensates for strain partitioning. The irregular shell morphology, stabilized by B2 pinning, promotes additional slip activation. This accommodates strain inhomogeneity and facilitates strain partitioning, leading to enhanced GND accumulation at interfaces. This mechanism further enhances strain hardening in the integral core-shell structure.

5. Conclusion

This study reports the successful development of an integral core-shell structure in a cast Ni-HEA through precise alloy composition design and TMP. The well-defined core-shell configuration, featuring an isotropic grain distribution, effectively addresses the strength-ductility trade-off typically encountered in HEAs. The bulged regions, acting as shells around coarse grains, allow uniform deformation while enhancing strain hardening owing to HDI strengthening. The presence of B2 and L12 precipitates in the bulged region further improves the mechanical stability of the alloy. During deformation, precipitates and grain/twin boundaries contribute to dislocation pile-up, leading to deformation incompatibility with the core region and significantly enhancing back stress strengthening. The integral core-shell structure reaches strain hardening rate of ~3.4 GPa. Additionally, our findings indicate that the scalability challenges of traditional PM processes, associated with the production of core-shell structures in HEAs, can be mitigated through casting and targeted TMP. Future work will focus on optimizing mechanical properties by precisely controlling TMP parameters to manage the shell fraction and size, thereby advancing the potential for industrial-scale applications of cast HEAs.

Declaration of competing interest

The authors declare that they have no known competing financial interestsor personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Hyojin Park: Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Qingfeng Wu:** Writing – review & editing, Validation, Investigation, Formal analysis. **Yoon–Uk Heo:** Validation, Methodology, Investigation. **Sun Ig Hong:** Writing – review & editing, Investigation. **Rae Eon Kim:** Methodology, Investigation, Data curation. **Do Won Lee:** Methodology, Investigation, Data curation, Investigation, Methodology, Investigation. **Zhe Gao:** Data curation, Investigation, Methodology. **Jae Heung Lee:** Methodology, Investigation. **Hyo Moon Joo:** Resources. **Jongun Moon:** Methodology, Investigation. **Young-Sang Na:** Methodology, Investigation. **Jae-il Jang:** Investigation, Methodology. **Hyoung Seop Kim:** Writing – review & editing, Supervision.

Acknowledgements

This research was supported by the Nano & Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (RS-2023–00281246). This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (NRF-2022R1A5A1030054). Q. Wu was supported by the Brain Pool Program through the National Research Foundation of Korea (NRF) (Grant No. RS–2023–00222130). This research was supported by the Hyundai Motor Group. The authors appreciate the Pohang Accelerator Laboratory (Pohang, Republic of Korea) for providing the synchrotron radiation sources at the 8D beamlines used in this study. The first author would like to thank Dr. Eun Seoung Kim for his contribution to the Thermo-Calc calculations, and Mr. Jaeik Kwak for the SEM analysis.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jmst.2025.04.017.

References

- [1] Y.H. Jo, J. Yang, W.M. Choi, K.Y. Doh, D. Lee, H.S. Kim, B.J. Lee, S.S. Sohn, S. Lee, J. Mater. Sci. Technol. 76 (2021) 222–230.
- [2] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent, Mater. Sci. Eng. A 375 (2004) 213–218.
- [3] J. Guo, B. Zhou, S. Qiu, H. Kong, M. Niu, J. Luan, T. Zhang, H. Wu, Z. Jiao, J. Mater. Sci. Technol. 166 (2023) 67–77.
- [4] D. Zhang, J. Zhang, J. Kuang, G. Liu, J. Sun, Acta Mater. 220 (2021) 117288.
- [5] F. Haftlang, J.B. Seol, A. Zargaran, J. Moon, H.S. Kim, Acta Mater. 256 (2023) 119115.
- [6] Z. Li, K.G. Pradeep, Y. Deng, D. Raabe, C.C. Tasan, Nature 534 (7606) (2016) 227–230.
- [7] H. Park, J. Lee, R.E. Kim, S. Son, S.Y. Ahn, H.S. Kim, Met. Mater. Int. 30 (3) (2024) 585–592.
- [8] X. Xu, Z. Song, K. Wang, H. Li, Y. Pan, H. Hou, Y. Zhao, J. Mater. Sci. Technol. 219 (2024) 307–325.
- [9] H.U. Jeong, N. Park, Mater. Sci. Eng. A 782 (2020) 138896.
- [10] S.J. Youn, Y.K. Kim, J.B. Seol, D.H. Chung, Y.S. Naet, Met. Mater. Int. (2024), doi:10.1007/s12540-024-01865-9.
 [11] L. Zhang, K. Guo, H. Tang, M. Zhang, J. Fan, P. Cui, Y. Ma, P. Yu, G. Li, Mater. Sci.
- Eng. A 757 (2019) 160–171.
- [12] H. He, J. Liao, Y. Xuan, H. Liu, W. Zhang, Z. Gong, M. Li, X. Wang, Mater. Chem. Phys. 318 (2024) 129214.

- [13] Y. Wang, M. Chen, F. Zhou, E. Ma, Nature 419 (6910) (2002) 912-915.
- [14] Z. Wang, J. Li, Y. Yang, L. Pang, M. Liu, H. Li, Q. Liu, B. Fu, Y. Guo, Z. Wang, Mater. Sci. Eng. A 870 (2023) 144851.
- [15] K. Ramkumar, H. Park, J. Lee, H. Kwon, R. Vikram, E.S. Kim, A. Zaragaran, H.S. Kim, Mater. Sci. Eng. A 885 (2023) 145606.
- [16] Q. Wu, F. He, J. Li, H.S. Kim, Z. Wang, J. Wang, Nat. Commun. 13 (1) (2022) 4697
- [17] M. Hasan, Y. Liu, X. An, J. Gu, M. Song, Y. Cao, Y. Li, Y. Zhu, X. Liao, Int. J. Plast. 123 (2019) 178-195.
- [18] J. Ding, Q. Li, J. Li, S. Xue, Z. Fan, H. Wang, X. Zhang, Acta Mater. 149 (2018) 57 - 67.
- [19] G. Li, M. Liu, S. Lyu, M. Nakatani, R. Zheng, C. Ma, Q. Li, K. Ameyama, Scr. Mater, 191 (2021) 196-201
- [20] B. Sharma, M. Miyakoshi, S.K. Vajpai, G. Dirras, K. Ameyama, Mater. Sci. Eng. A 797 (2020) 140227
- [21] Y. Zhu, K. Ameyama, P.M. Anderson, I.J. Beyerlein, H. Gao, H.S. Kim, E. Lavernia, S. Mathaudhu, H. Mughrabi, R.O. Ritchie, Mater. Res. Lett. 9 (1) (2021) 1-31.
- [22] P. Sathiyamoorthi, H.S. Kim, Prog. Mater. Sci. 123 (2022) 100709.
- [23] K. Ameyama, F. Cazes, H. Couque, G. Dirras, S. Kikuchi, J. Li, F. Mompiou,
- K. Mondal, D. Orlov, B. Sharma, Mater. Res. Lett. 10 (7) (2022) 440-471. [24] S.K. Vajpai, C. Sawangrat, O. Yamaguchi, O.P. Ciuca, K. Ameyama, Mater. Sci. Eng. C 58 (2016) 1008-1015.
- [25] S. Du, T.W. Zhang, Z.M. Jiao, D. Zhao, J.J. Wang, R.L. Xiong, H.S. Kim, Z.H. Wang, Scr. Mater. 235 (2023) 115635.
- [26] P.A. Beck, P.R. Sperry, J. Appl. Phys. 21 (2) (1950) 150-152.
- [27] K. Huang, Towards the Modelling of Recrystallization Phenomena in Multi-Pass conditions: Application to 304L Steel, École Nationale Supérieure des Mines de Paris, 2011.
- [28] S. Pradhan, S. Mandal, C. Athreya, K.A. Babu, B. De Boer, V.S. Sarma, Mater. Sci. Eng. A 700 (2017) 49-58.
- [29] X. Zhong, L. Huang, F. Liu, J. Mater. Eng. Perform. 29 (2020) 6155-6169.
- [30] J. Wang, H. Kwon, H.S. Kim, B.J. Lee, NPJ Comput. Mater. 9 (1) (2023) 60.
- [31] B. Gwalani, V. Soni, D. Choudhuri, M. Lee, J. Hwang, S. Nam, H. Ryu, S.H. Hong, R. Banerjee, Scr. Mater. 123 (2016) 130-134.
- [32] T.T. Shun, Y.C. Du, J. Alloy. Compd. 479 (2009) 157-160.
- [33] L. Lan, H. Yang, R. Guo, X. Wang, M. Zhang, P. Liaw, J. Qiao, Mater. Chem. Phys. 270 (2021) 124800.
- [34] Y. Zhao, Y. Guo, Q. Wei, T. Topping, A. Dangelewicz, Y. Zhu, T. Langdon, E. Lavernia, Mater. Sci. Eng. A 525 (2009) 68-77.
- [35] G. Ribárik, B. Jóni, T. Ungár, Crystals 10 (7) (2020) 623.
- [36] N. Bibhanshu, S. Suwas, J. Mater. Res. 35 (13) (2020) 1635-1646.
- [37] J.H. Lee, J. Lee, H. Kwon, H. Park, E.S. Kim, Y.U. Heo, H.S. Kim, Mater. Sci. Eng. A 895 (2024) 146247.
- [38] J. Lee, S.I. Hong, H.S. Kim, Int. J. Plast. 185 (2025) 104224
- [39] D. Duly, Y. Brechet, Acta Metall. Mater. 42 (1994) 3035-3043.
- [40] M. Perez, M. Dumont, D. Acevedo-Reyes, Acta Mater. 56 (2008) 2119-2132.
- [41] Y. Tian, L. Zhao, S. Chen, A. Shibata, Z. Zhang, N. Tsuji, Sci. Rep. 5 (2015) 16707.
- [42] E. Brünger, X. Wang, G. Gottstein, Scr. Mater. 38 (1998) 1843-1849.
- [43] S. Mandal, A. Bhaduri, V.S. Sarma, Metall. Mater. Trans. A 43 (2012) 2056–2068. [44] A. Emdadi, Y. Yang, S. Bolz, O. Stryzhyboroda, M. Tovar, S. Gein, U. Hecht, S. Weiß, Scr. Mater. 237 (2023) 115705.
- [45] B.C. Xie, Y.W. Luo, Z.T. Wang, Q.Q. Meng, Y.Q. Ning, M.W. Fu, J. Mater. Sci. Technol. 322 (2024) 78-91.

- [47] R.R. Eleti, A.H. Chokshi, A. Shibata, N. Tsuji, Acta Mater. 183 (2020) 64-77.
- [48] Y. Iin, B. Lin, M. Bernacki, G.S. Rohrer, A. Rollett, N. Bozzolo, Mater, Sci. Eng, A 597 (2014) 295-303.
- [49] F. Han, B. Tang, H. Kou, J. Li, Y. Feng, J. Mater. Sci. 48 (2013) 7142-7152.
- [50] S. Chatterjee, Y. Li, G. Po, Int. J. Plast. 145 (2021) 103062.
- [51] P. Changizian, Z. Yao, M. Daymond, Mater. Charact. 172 (2021) 110891. [52] M.Y. Sung, T.J. Jang, S.Y. Song, G. Lee, K. Ryou, S.H. Oh, B.J. Lee, P.P. Choi,
- J. Neugebauer, B. Grabowski, J. Mater. Sci. Technol. 225 (2024) 72-86.
- [53] H. Park, S. Son, S.Y. Ahn, H. Ha, R.E. Kim, J.H. Lee, H.M. Joo, J.G. Kim, H.S. Kim, Mater. Res. Lett. 13 (4) (2025) 348-356.
- [54] T. Li, D. Wang, J. Cui, Q. Wang, S. Zhang, J. Wang, J. Mater. Sci. Technol. 208 (2025) 53-66.
- [55] H. Park, F. Haftlang, Y.U. Heo, J.B. Seol, Z. Wang, H.S. Kim, Nat. Commun. 15 (1) (2024) 5757.
- [56] J. Hou, S. Liu, B. Cao, J. Luan, Y. Zhao, Z. Chen, Q. Zhang, X. Liu, C. Liu, J. Kai, Acta Mater. 238 (2022) 118216.
- S. Luo, T. Zhang, H. Chang, S. Du, Z. Jiao, R. Xiong, H.S. Kim, Z. Wang, J. Mater. [57] Res. Technol. 25 (2023) 3093-3103.
- [58] E. Hall, Proc. Phys. Soc. B 64 (9) (1951) 747.
- [59] N.J. Petch, J. Iron Steel Inst. 174 (1953) 25-28.
- [60] L. Fan, T. Yang, Y. Zhao, J. Luan, G. Zhou, H. Wang, Z. Jiao, C.T. Liu, Nat. Commun. 11 (1) (2020) 6240.
- [61] J. Bailey, P. Hirsch, Philos. Mag. 5 (53) (1960) 485-497.
- [62] Y. Zhao, T. Yang, Y. Tong, J. Wang, J. Luan, Z. Jiao, D. Chen, Y. Yang, A. Hu, C. Liu, Acta Mater. 138 (2017) 72-82.
- [63] K. Ming, X. Bi, J. Wang, Int. J. Plast. 100 (2018) 177-191.
- [64] A.J. Ardell, Metall. Trans. A 16 (1985) 2131-2165
- [65] T. Pollock, A. Argon, Acta Metall. Mater. 40 (1992) 1-30.
- [66] M. Yang, Y. Pan, F. Yuan, Y. Zhu, X. Wu, Mater. Res. Lett. 4 (2016) 145-151.
- [67] Z.S. Toor, J. Kwon, R.E. Kim, Y.T. Choi, G.H. Gu, M.H. Seo, K.H. Chung, R. Wu, H.S. Kim, Met. Mater. Int. 31 (2025) 994-1008.
- [68] X. Gao, R. Chen, T. Liu, G. Qin, J. Guo, Mater. Sci. Eng. A 860 (2022) 144296.
- [69] X. Liu, Q. Xue, W. Wang, L. Zhou, P. Jiang, H. Ma, F. Yuan, Y. Wei, X. Wu, Materialia 7 (2019) 100376.
- [70] X. Fang, G. He, C. Zheng, X. Ma, D. Kaoumi, Y. Li, Y. Zhu, Acta Mater. 186 (2020) 644-655.
- [71] H. Jung, S. Lee, T. Kang, A. Zargaran, P.P. Choi, S.S. Sohn, J. Mater. Sci. Technol. 181 (2024) 71-81.
- [72] W. Lu, K. Yan, X. Luo, Y. Wang, L. Hou, P. Li, B. Huang, Y. Yang, J. Mater. Sci. Technol. 98 (2022) 197-204.
- [73] H. Kwon, E.S. Kim, Y.U. Heo, J. Choe, R.E. Kim, S.Y. Ahn, S.H. Oh, J.M. Park, B.J. Lee, H.S. Kim, J. Mater. Sci. Technol. 214 (2025) 143-152.
- [74] S.I. Hong, C. Laird, Acta Metall. Mater. 38 (1990) 1581-1594.
- [75] C. Yang, Z. Zhang, T. Cai, P. Zhang, Z. Zhang, Sci. Rep. 5 (2015) 15532.
- [76] H. Gao, Y. Huang, W.D. Nix, J. Hutchinson, J. Mech. Phys. Solids 47 (1999) 1239-1263
- [77] S. Hong, M. Hill, Acta Mater. 46 (1998) 4111-4122.
- [78] M. Calcagnotto, D. Ponge, E. Demir, D. Raabe, Mater. Sci. Eng. A 527 (2010) 2738-2746.
- [79] C. Wagner, A. Ferrari, J. Schreuer, J.P. Couzinié, Y. Ikeda, F. Körmann, G. Eggeler, E.P. George, G. Laplanche, Acta Mater. 227 (2022) 117693.
- [80] M.B. Kivy, M.A. Zaeem, Scr. Mater. 139 (2017) 83-86.
- [81] N. Xu, Z. Yang, X. Mu, Y. Huang, S. Li, Y.D. Wang, Appl. Phys. Lett. 119 (2021) 261902.

- [46] I. Ovid'Ko, N. Skiba, Int. J. Plast. 62 (2014) 50-71.