Scripta Materialia 253 (2024) 116289

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.journals.elsevier.com/scripta-materialia

Moderate rolling for producing effective heterostructure

R. Zhou [a,b], J. Yan [b], H. Tao [a], X.L. Ma [b], X.P. Liang [a,*], Y. Liu [c], Y.T. Zhu [b,*]

[a] School of Materials Science and Engineering, Central South University, Changsha 410083, PR China
[b] Department of Materials Science and Engineering, Hong Kong Institute for Advanced Study, City University of Hong Kong, Kowloon, Hong Kong, China
[c] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, PR China

ARTICLE INFO

Keywords:
Heterostructured materials
Rolling strain
HDI strengthening
Medium entropy alloys

ABSTRACT

Severe cold rolling followed by recrystallization has been widely used to produce heterostructures for superior strength-ductility combinations in metallic materials. However, this requires a thick feeding stock and has high processing cost due to severe rolling strain. Here we report that only moderate rolling is needed to produce an effective heterostructure for high yield strength and good ductility in FeCrNi medium entropy alloys (MEA). Moderate rolling plus partial recrystallization produces a unique heterostructure, in which the recrystallized zones is harder than the unrecrystallized zones. This is formed by a mechanism that is very different from what is reported for severely cold-rolled metals. The strategy developed here has notable advantages in terms of high efficiency, low cost, and superior mechanical properties, rendering it applicable for a wide range of alloy systems.

Heterostructured (HS) materials, characterized by distinct constituent zones at appropriate length scales, has emerged as a novel microstructure strategy for designing metals and alloys with attractive combination of strength and ductility [1–9]. At the heart of HS strategy is the interactive coupling between hard and soft zones with dissimilar mechanical properties to generate local but substantial strain gradients accommodated by geometrically necessary dislocations (GNDs) during deformation [1,10]. Such interaction between HS zones leverages the hetero-deformation induced (HDI) strengthening and work hardening, whose potential is rather low in conventional homogeneous microstructure [1,11]. Consequently, if not intrinsically brittle, HS materials often outperform their homogeneous counterparts in strength-ductility combinations [12–14].

One of the primary methodologies to process HS materials is to combine severe cold rolling with a total reduction of usually above 85 % and appropriate subsequent heat treatment [15]. For example, a heterostructured CoCrFeMnNi high entropy alloys was processed by severe cold rolling (reduction ratio ~ 96.7 %) plus partial recrystallization, which produced a high yield strength of 827 MPa while retaining a good ductility of 12.9 % [16]. The underlying principle is to impart high defect densities through severe rolling deformation, which suffices the thermodynamic driving force for partial or non-uniform recrystallization in subsequent annealing. As a result, the unrecrystallized regions with small grain sizes serve as the hard zones whereas the recrystallized regions as the soft zones. The strength and flow behavior of such as-processed hard and soft zones can be different by a large margin, thereby promoting the HDI effect to enhance the overall mechanical properties of the materials [17].

The convention of severe cold rolling to fabricate HS materials at research laboratories is a natural continuation of the decades-long research in severe plastic deformation to produce ultrafine-grained materials [18,19]. Ultrafine grains are usually the desired hard zones in the HS materials processed by cold deformation and subsequent annealing. However, the severe-rolling-based approach could be equipment demanding and energy consuming, thus presents a low cost-effectiveness for commercial scale production. It is thus worthwhile to explore processing routes that is less rolling-intensive but capable of producing effective heterostructure with equal or even better mechanical performance.

From the perspective of microstructure development, recrystallization is not necessarily the sole path to heterogeneous grain structures using cold rolling and subsequent heat treatment. Deformation during cold rolling itself is non-homogeneous at the early to intermediate rolling stages, thus allowing microstructure manipulation towards HS constituent zones when coupled with post-rolling heat treatment. Experimental endeavors in this regime are relatively scarce but expected to deliver more efficient and eco-friendly processing technologies for HS materials. Moreover, there are also critical scientific questions pertinent

* Corresponding authors.
E-mail addresses: xpliang@csu.edu.cn (X.P. Liang), y.zhu@cityu.edu.hk (Y.T. Zhu).

https://doi.org/10.1016/j.scriptamat.2024.116289
Received 4 June 2024; Received in revised form 22 July 2024; Accepted 29 July 2024
Available online 8 August 2024
1359-6462/

to the issue. For example, if this proposed low rolling-intensive route is viable, is there a lower limit for thickness reduction to attain heterostructures with decent mechanical properties and what is the underlying microstructure physics?

In this paper, we explore the potential of moderate rolling to produce heterostructured materials with desired strength and ductility, using an FeCrNi medium entropy alloy (MEA) as an example. The role of thickness reduction on the development of heterostructure after heat treatment is carefully examined, and its impact on mechanical performance is discussed in detail. We also investigated the lower limit for thickness reduction, below which the as-processed material becomes intrinsically more brittle due to the retention of much coarse grains structure. The results suggests that a window of moderate rolling reduction is preferred in processing to achieve heterostructures with an outstanding strength-ductility combination. A novel type of heterostructure was developed in this study, in which the recrystallized fine-grained zones have higher strength than large unrecrystallized zones, contrary to the reported heterostructures produced by severe cold rolling and annealing, in which the recrystallized zones act as softer zones. This study advances the understanding of processing strategies for achieving superior mechanical properties in HS materials.

The FeCrNi medium entropy alloy (MEA) was fabricated using the Hot Isostatic Pressing (HIP) technique. Raw materials of Fe, Cr, and Ni with high purity (>99.99 %) were melted in a tungsten crucible and subsequently atomized under Ar gas at 4 MPa. The resulting powder was compacted in a stainless steel can and subjected to degassing and solidification processes at 140 MPa and 1200 °C for 2 h. Following HIP treatment, the billet was cooled to room temperature in a furnace and further processed into sheets of varying thicknesses (as shown in Fig. S1). Cold rolling was performed on sheets with different initial thickness of 2, 3, 4, and 8 mm to a final thickness of 1.2 mm, corresponding to rolling reductions of 40 %, 60 %, 70 %, and 85 % (rolling strains ε of 0.7, 1.5, 2.3, and 5.7). These samples were denoted as MEA40, MEA60, MEA70, and MEA85, respectively. A pilot testing of hardness on each cold-rolled sample after a series of heat treatments (different temperatures for 1 h) is done to determine the appropriate heat treatment conditions (Fig. 1). All samples exhibit a nearly identical hardness level after 700 °C annealing for 1 h, suggesting their strength are rather similar regardless of different rolling reductions. Therefore, this heat treatment condition enables a valid evaluation of mechanical properties (strength-ductility combination) under the same cost of heat treatment.

Thus, all samples were heat-treated at 700 °C for 1 h, followed by being shaped into dog-bone specimens with a gauge length of 10 mm

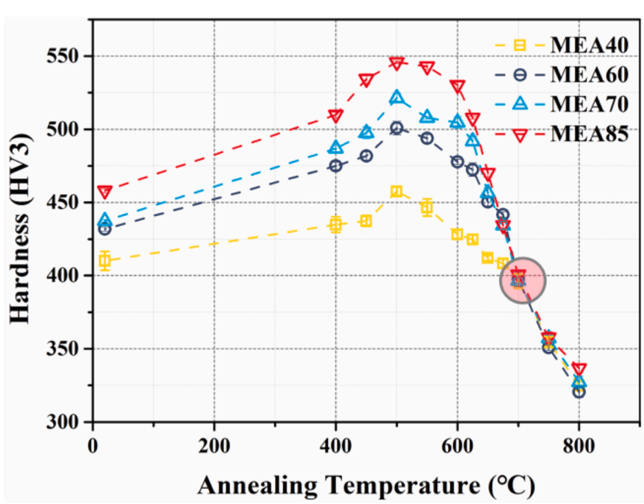

Fig. 1. Hardness variation curves of FeCrNi MEA with different rolling reduction under loading level of 3 kg.

and a width of 3 mm. Uniaxial tensile tests were performed using a Shimazu testing machine at a strain rate of 1 × 10^{-3} s^{-1} and at room temperature. Each sample was tested a minimum of three times to ensure data reproducibility. Additionally, loading-unloading-reloading (LUR) tests were conducted to measure the hetero-deformation-induced (HDI) stress at the same strain rate. Field-emission scanning electron microscopy (SEM) equipped with an electron back-scattered diffraction (EBSD) detector was utilized to investigate the microstructural differences and fracture morphologies associated with varying cold rolling reductions.

Figs. 2 and S2 show the heterostructure characteristics of moderate-rolled samples (MEA60 and MEA70) after annealing, in contrast with the severely rolled one (MEA85). For moderate-rolled samples, grain structures can be clearly classified into two zones (Fig. 2a and b) – one embraces fine grains of a few micrometers and the other contains relatively larger grains with their sizes above ten micrometers (Fig. 2d and e).

The moderate rolling produced a novel type of heterostructure with recovered coarse-grained regions as the soft zones, and recrystallized fine -grained regions as the hard zones (shown in Fig. S3), which is opposite to the heterostructure produced by severe-rolling-based route [15,16]. This is because the formation pathway for the present heterostructure is distinctively different from those early reports based on severe-rolling-based routes. According to the grain boundary characteristics (Fig. 2g and h), the fine grain boundaries are primarily of high angle, because they were produced by recrystallization of more severely deformed regions. Instead, the large, grained zones did not come from recrystallization. They are originated from coarse grains whose grain refinement is incomplete upon moderate rolling. Despite some extent of recovery during the heat treatment, the remanence of intragranular dislocations is appreciable (Fig. 3a and b). In contrast, MEA85 sample exhibits almost uniformly recrystallized fine grains, far from the development of an effective heterostructure. This is because the increased rolling reduction led to a more uniform accumulation of plastic strain within the initial microstructure, thereby promoting the homogenization of microstructures. Conventional wisdom of processing to obtain heterostructure is to further prolong annealing by stimulating abnormal grain growth.

Fig. 4a shows that both MEA60 and MEA70 exhibit comparable yield strength to MEA85, which is consistent with the prior hardness testing but in contrast to their different average grain sizes. The unexpected high tensile strength in heterostructures (MEA60 and MEA70) can be attributed to the enhanced strain hardening [20]. Since hardness/strength is kept similar in the design of heat treatment, the ductility is of interest in terms of property comparison. Notably, both heterostructured samples demonstrate significantly enhanced fracture elongation and uniform elongation (marked circle in Fig. 4a and b) compared to the MEA85 sample. Further details regarding the tensile properties of the FeCrNi MEA can be found in Table S1. The enhanced ductility of MEA60 and MEA70 can be attributed to their significantly higher work hardening rate (Θ), as depicted in Fig. 4c.

The enhanced strain hardening rate and ductility can be elucidated by the hetero-deformation-induced stress during plastic deformation [21]. The dissimilar grain sizes and intragranular dislocation densities in different zones of MEA60 and MEA70 lead to considerable mechanical incompatibility during deformation, inducing local strain gradient and effective accumulation of GNDs to improve strain hardening rate. This HDI stress and hardening is substantial compared to the homogeneous sample (MEA85), as evidenced by the loading-unloading-reloading measurement in Fig. S4. It can be deduced that the initial remanence of intragranular dislocations in heterostructured samples after annealing does not consume much the room for subsequent dislocation storage. Thus, the moderate-rolling induced heterostructures can leverage the potential of HDI effect comparable to those from conventional rolling-intensive routes.

In the rest following, we show and discuss the existence of a lower

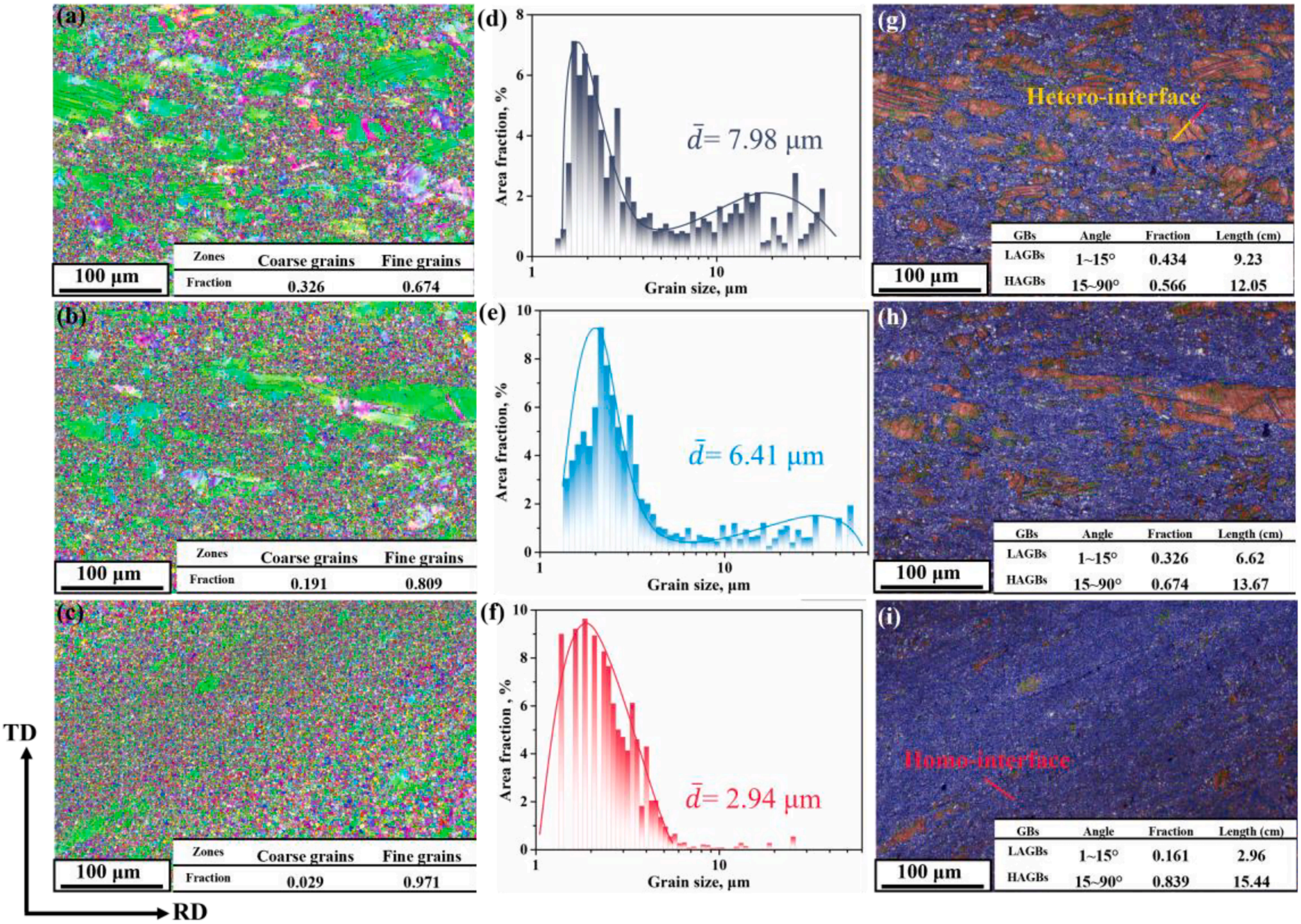

Fig. 2. EBSD images of FeCrNi MEA with different cold rolling reduction followed by annealing at 700 °C for 1 h. (a–c) inverse pole figures (IPF). Red, green and blue color represents (001), (101) and (111) poles respectively. (d–f) grain size distributions maps, and (g–i) low & high angle boundaries maps of MEA60, MEA70 and MEA85. Blue and red lines represent high and low angle boundaries respectively.

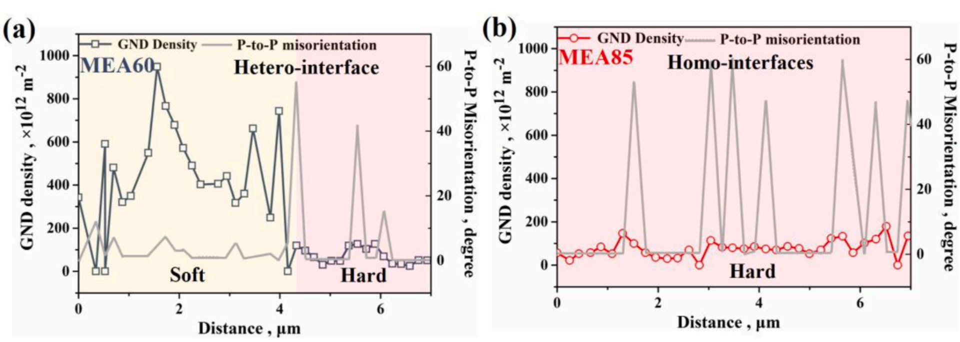

Fig. 3. (a, b) Dislocation density distributions across the heterostructure-interface in MEA60 and homogenous-interface in MEA85.

limit for rolling reduction, below which the formation of effective heterostructure for property improvement is not successful. Fig. 5a–c presents the microstructures and tensile properties of MEA40, with MEA60 as a benchmark for property. MEA40 also exhibits heterostructure with respective zones of recrystallized fine grains and deformed large grains, resembling features in MEA60 except largely different zone volume fractions. Nevertheless, MEA40 exhibits a much-limited elongation to failure, i.e., the heterostructure formed in MEA40 is not effective in improving the ductility.

Fundamentally, the ductility of materials is determined by two competing factors – the strain hardening rate drops to the level of flow stress to initiate necking instability (Considère criterion), or the flow stress reaches the level for crack nucleation and propagation – whichever comes first upon loading. Considering Considère criterion $\frac{\partial\sigma}{\partial\varepsilon} = \sigma$ and assuming hardening behavior can be approximated by Hollomon equation $\sigma = K\varepsilon^n$, where σ and ε represent the true stress and strain, respectively, obtained from tensile tests; K is a constant; and n is the work hardening index [22]. Thus, the uniform elongation strain upon necking failure can be estimated as n.

Fig. 5d presents the lnσ-lnε curves of MEA40 and MEA60, demonstrating a much similar working hardening index (0.122 for MEA40 and 0.126 for MEA60). Thus, necking instability is not the governing factor

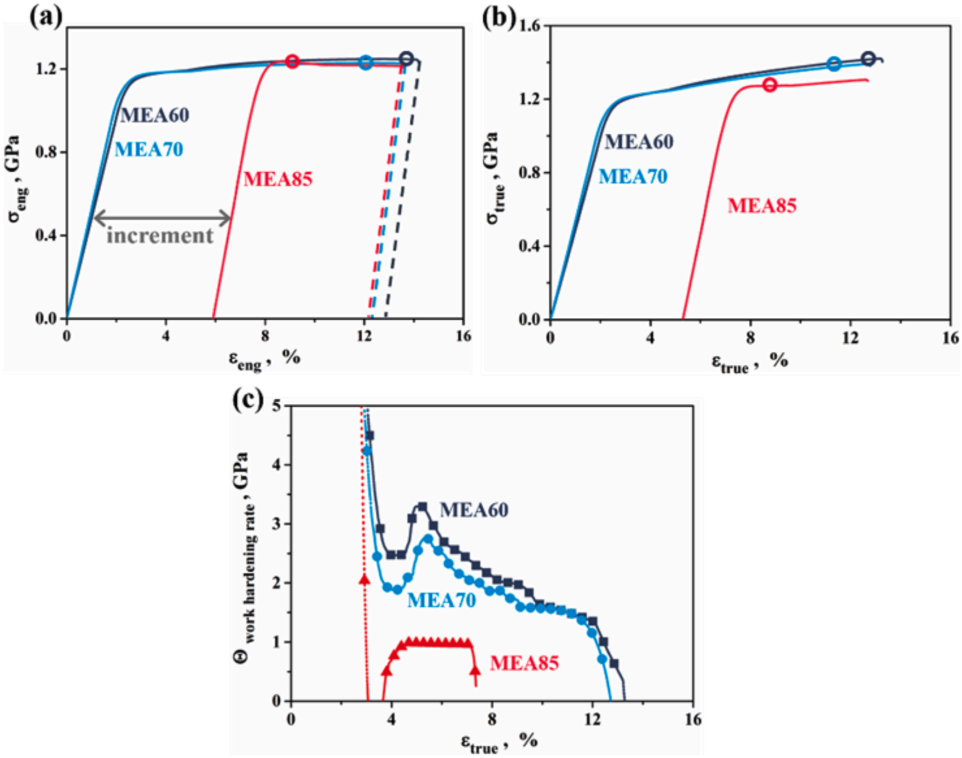

Fig. 4. Tensile properties of FeCrNi MEA with varying cold rolling reduction. (a) Engineering stress-strain curves, (b) true stress-strain curves, and (c) work hardening rate versus true strain curves for MEA60, MEA70, and MEA85.

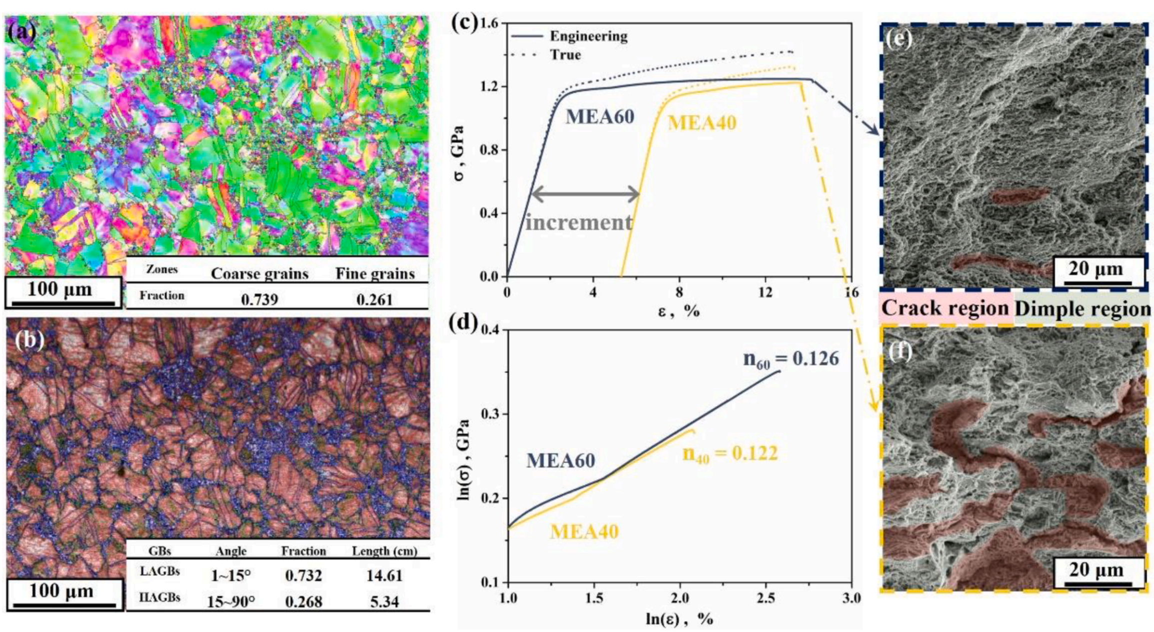

Fig. 5. Comparison of microstructures and tensile properties between MEA40 and MEA60. (a) IPF. Red, green and blue color represents (001), (101) and (111) poles respectively. (b) low & high angle boundaries map of MEA40. (c) Engineering/True stress-strain curves, (d) ln(σ) versus ln(ε) curves, (e, f) tensile fracture morphologies of MEA60 and MEA40. Blue and red lines represent high and low angle boundaries respectively.

for the failure of MEA40 since its failure strain (6.2 %) is unproportionally lower than that of MEA60 (9.1 %). It can be inferred that the crack nucleation and growth caused premature failure and diminished ductility in MEA40. The fracture morphologies of MEA40 (Fig. 5f) reveal extensive regions of crack propagation, indicating brittleness induced by the inadequate crack resistance of the large-grain boundaries. In contrast, the fracture morphologies of MEA60 (Fig. 5e) exhibit a predominant dimple-like region, indicating superior crack resistance and higher ductility. Therefore, below a critical rolling reduction, the heat treatment with identical energy input is incapable of producing effective heterostructure due to the significant retention of large grains whose boundaries are susceptible to crack propagation.

In summary, it is demonstrated that moderate rolling can be applied to produce a novel and effective heterostructure to improve mechanical properties with high efficiency and low cost. The recrystallized fine grains formed hard zones and the deformed large grains formed soft zones, which enabled the potential of HDI effect as effective as microstructures from rolling-intensive routes. Meanwhile, it is found that rolling reduction to enable such strategy has a lower limit, below which over-retention of large grains is undesired and drives the failure by crack nucleation and propagation along grain boundaries. Therefore, moderate rolling reduction coupled with appropriate annealing is indicated as an effective and economical processing route for production of heterostructure materials for superb combination of strength and ductility. This strategy can be widely applied to produce heterostructures through the non-uniform accumulation of plastic strain during moderate cold rolling, regardless of the material.

CRediT authorship contribution statement

R. Zhou: Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **J. Yan:** Validation. **H. Tao:** Validation. **X.L. Ma:** Writing – review & editing. **X.P. Liang:** Validation, Methodology, Conceptualization. **Y. Liu:** Writing – review & editing, Resources. **Y.T. Zhu:** Writing – review & editing, Supervision, Resources, Funding acquisition.

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.

Acknowledgments

This work is supported by the National Key R&D Program of China (2021YFA1200202), National Natural Science Foundation of China (51931003), Hong Kong Research Grants Council (GRF 11214121).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.scriptamat.2024.116289.

References

[1] Y. Zhu, X. Wu, Heterostructured materials, Prog. Mater Sci. 131 (2023) 101019.
[2] Z. An, S. Mao, C. Jiang, Z. Li, S. Wu, Y. Zhai, L. Wang, Y. Liu, Z. Zhang, X. Han, Achieving superior combined cryogenic strength and ductility in a high-entropy alloy via the synergy of low stacking fault energy and multiscale heterostructure, Scr. Mater. 239 (2024) 115809.
[3] D. Wu, M. Hao, T. Zhang, Z. Wang, J. Wang, G. Rao, L. Zhang, C. Ding, K. Zhou, L. Liu, Heterostructures enhance simultaneously strength and ductility of a commercial titanium alloy, Acta Mater. 257 (2023) 119182.
[4] Z. Luo, J. Li, T. Feng, K. Lu, X. Ma, Optimizing heterostructure parameters for enhanced mechanical performance of Al0.1CoCrFeNi high entropy alloy, Mater. Sci. Eng. A 885 (2023) 145623.
[5] R.E. Kim, E.S. Kim, G.M. Karthik, G.H. Gu, S.Y. Ahn, H. Park, J. Moon, H.S. Kim, Heterostructured alloys with enhanced strength-ductility synergy through laser-cladding, Scr. Mater. 215 (2022) 114732.
[6] T. Chou, W. Li, H. Chang, B. Cao, J. Luan, J. Huang, T. Yang, Suppressing temperature-dependent embrittlement in high-strength medium-entropy alloy via hetero-grain/precipitation engineering, Scr. Mater. 229 (2023) 115377.
[7] J. Peng, L. Li, F. Li, B. Liu, S. Zherebtsov, Q. Fang, J. Li, N. Stepanov, Y. Liu, F. Liu, The predicted rate-dependent deformation behaviour and multistage strain hardening in a model heterostructured body-centered cubic high entropy alloy, Int. J. Plast. 145 (2021) 103073.
[8] X. Liu, S. Zhang, H. Feng, J. Wang, P. Jiang, H. Li, F. Yuan, X. Wu, Outstanding fracture toughness combines gigapascal yield strength in an N-doped heterostructured medium-entropy alloy, Acta Mater. 255 (2023) 119079.
[9] G. Karthik, Y. Kim, E.S. Kim, A. Zargaran, P. Sathiyamoorthi, J.M. Park, S.G. Jeong, G.H. Gu, A. Amanov, T. Ungar, Gradient heterostructured laser-powder bed fusion processed CoCrFeMnNi high entropy alloy, Addit. Manuf. 59 (2022) 103131.
[10] Y. Zhu, K. Ameyama, P.M. Anderson, I.J. Beyerlein, H. Gao, H.S. Kim, E. Lavernia, S. Mathaudhu, H. Mughrabi, R.O. Ritchie, Heterostructured materials: superior properties from hetero-zone interaction, Mater. Res. Lett. 9 (1) (2021) 1–31.
[11] Z. Fu, B.E. MacDonald, Z. Li, Z. Jiang, W. Chen, Y. Zhou, E.J. Lavernia, Engineering heterostructured grains to enhance strength in a single-phase high-entropy alloy with maintained ductility, Mater. Res. Lett. 6 (11) (2018) 634–640.
[12] X. Wu, Y. Zhu, Heterogeneous materials: a new class of materials with unprecedented mechanical properties, Mater. Res. Lett. 5 (8) (2017) 527–532.
[13] X. Wu, M. Yang, F. Yuan, G. Wu, Y. Wei, X. Huang, Y. Zhu, Heterogeneous lamella structure unites ultrafine-grain strength with coarse-grain ductility, Proc. Natl. Acad. Sci. 112 (47) (2015) 14501–14505.
[14] Y. Zhu, Introduction to heterostructured materials: a fast emerging field, Metall. Mater. Trans. A 52 (11) (2021) 4715–4726.
[15] J. Li, Y. Cao, B. Gao, Y. Li, Y. Zhu, Superior strength and ductility of 316L stainless steel with heterogeneous lamella structure, J. Mater. Sci. 53 (14) (2018) 10442–10456.
[16] P. Wang, J. Chen, B. Sun, D. Zhu, Y. Cao, Effects of annealing process parameters on microstructural evolution and strength-ductility combination of CoCrFeMnNi high-entropy alloy, Mater. Sci. Eng. A 840 (2022) 142880.
[17] J. Li, Q. Zhang, R. Huang, X. Li, H. Gao, Towards understanding the structure–property relationships of heterogeneous-structured materials, Scr. Mater. 186 (2020) 304–311.
[18] I. Ovid'Ko, R. Valiev, Y. Zhu, Review on superior strength and enhanced ductility of metallic nanomaterials, Prog. Mater. Sci. 94 (2018) 462–540.
[19] R.Z. Valiev, Y. Estrin, Z. Horita, T.G. Langdon, M.J. Zehetbauer, Y. Zhu, Producing bulk ultrafine-grained materials by severe plastic deformation: ten years later, JOM 68 (2016) 1216–1226.
[20] X. Wu, P. Jiang, L. Chen, F. Yuan, Y.T. Zhu, Extraordinary strain hardening by gradient structure, Proc. Natl. Acad. Sci. U. S. A. 111 (20) (2014) 7197–7201.
[21] Y. Zhu, X. Wu, Perspective on hetero-deformation induced (HDI) hardening and back stress, Mater. Res. Lett. 7 (10) (2019) 393–398.
[22] B. Hornbuckle, C. Kale, S. Srinivasan, T. Luckenbaugh, K. Solanki, K. Darling, Revealing cryogenic mechanical behavior and mechanisms in a microstructurally-stable, immiscible nanocrystalline alloy, Scr. Mater. 160 (2019) 33–38.