



异构金属材料及其塑性变形与应变硬化

武晓雷¹ 朱运田^{2,3}

- 1 中国科学院力学研究所 非线性力学国家重点实验室 北京 100190
2 香港城市大学 材料科学与工程系 香港 999077
3 中国科学院金属研究所 沈阳材料科学国家研究中心 沈阳 110016

摘要 金属材料异构(heterostructure)是将具有显著流变应力差异的软硬相间区域作为基元进行有序构筑而成的微观组织,是旨在提高应变硬化能力和拉伸塑性的微结构设计策略,迄今应用于各种金属结构材料并获得了强度与塑性/韧性等力学性能的优异匹配。异构策略的出发点是其特征的力学响应,即塑性变形时在异构基元界面形成的应变梯度,异构的特征应力应变响应是力学迟滞环。相比均质结构中主导的林位错塑性和林硬化,异构为了协调界面应变梯度而产生几何必需位错,新增了基于几何必需位错的异质塑性变形并引起额外的应变硬化与额外的强化。本文综述了近期异构金属材料的研究进展,首先定义了异构中基元并据此把异构分类为基元异构、亚基元异构以及复合异构,随后分析并讨论了异构塑性变形时界面和位错等微结构演化,以及异质塑性变形、应变硬化和强化行为,最后展望了异构提升宏观力学性能匹配的潜力。

关键词 异构,异构基元,应变梯度,几何必需位错,应变硬化,塑性,梯度结构,层状结构

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Heterostructured Metallic Materials: Plastic Deformation and Strain Hardening

WU Xiaolei¹, ZHU Yuntian^{2,3}

*1 State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics,
Chinese Academy of Sciences, Beijing 100190, China*

2 Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong 999077, China

*3 Shenyang National Laboratory of Materials Science, Institute of Metal Research,
Chinese Academy of Sciences, Shenyang 110016, China*

Correspondent: WU Xiaolei, professor, Tel: 18910271505, E-mail: xlwu@imech.ac.cn

ZHU Yuntian, professor, Tel: (00852)90919934, E-mail: y.zhu@cityu.edu.hk

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ABSTRACT Strong and tough metallic materials are desired for light-weight structural applications in transportation and aerospace industries. Recently, heterostructures have been found to possess unprecedented strength-and-ductility synergy, which is until now considered impossible to achieve. Heterostructured metallic materials comprise heterogeneous zones with dramatic variations (> 100%) particularly in

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作者简介 武晓雷,男,1965年生,研究员,博士

通讯作者 武晓雷, xlwu@imech.ac.cn, 从事金属结构材料的力学行为与微结构机理研究
朱运田, y.zhu@cityu.edu.hk, 从事金属结构材料变形机理及性能研究

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mechanical properties. The interaction in these hetero-zones produces a synergistic effect wherein the integrated property exceeds the prediction by the rule-of-mixtures. More importantly, the heterostructured materials can be produced by current industrial facilities at large scale and low cost. The superior properties of heterostructured materials are attributed to the heterodeformation induced (HDI) strengthening and strain hardening, which is produced by the piling-up of geometrically necessary dislocations (GNDs). These GNDs are needed to accommodate the strain gradient near hetero-zone boundaries, across which there is high mechanical incompatibility and strain partitioning. This paper classifies the types of heterostructures and delineates the deformation behavior and mechanisms of heterostructured materials.

KEY WORDS heterostructure, heterostructure unit, strain gradient, geometrically necessary dislocation, strain hardening, ductility, gradient structure, lamellar structure

一代材料一代性能,高力学性能化是金属结构材料的永恒追求。金属结构材料升级的一个重要标志是不断提升的屈服强度等级^[1,2],而拉伸均匀伸长率,即拉伸塑性,是结构材料的另一个关键力学性能。然而,强度与拉伸塑性之间总是呈相互矛盾的倒置关系^[3],即拉伸塑性随强度的提高而降低^[4-12];特别地,低塑性在高强度下尤为凸显,并成为金属结构材料高力学性能化的主要瓶颈,提高应变硬化能力与拉伸塑性的高强度微结构设计成为金属材料强韧化研究的前沿和热点^[13-22]。

金属结构材料的强化提高屈服强度,应变硬化提高塑性^[23],传统强化与应变硬化的微观机制均为林位错塑性^[23],即位错的形成、储存、增殖与交互作用。利用晶界强化和形变强化等,得到高强度的纳米及超细晶结构^[6,10,11],往往还在晶粒内部储存了高密度位错,这些位错提前消耗了林硬化(forest hardening)、即减弱了随后的塑性变形和应变硬化能力。根据 Considère 判据,这些高强度微结构在小应变时应变硬化率就赶不上流变应力而无法持续进行均匀变形,因而林硬化能力的不足是其低塑性的原因^[10,11],这导致了快速发生应变局部化失稳,即颈缩。本质上,强度与拉伸塑性之间的协同关系是基于林位错塑性的强化与应变硬化的相互竞争和演化,迄今提升应变硬化能力的微结构设计策略包括利用纳米析出^[22]、第二相^[19]、相变^[15]、孪晶^[9]以及晶粒细化^[20]等,其核心都是增强林位错塑性,即通过形成和存储位错,阻碍位错滑移、促进位错交互作用,然而这些策略对于高强度结构却具有相当的挑战性^[6-9]。

旨在提升高强度金属材料的拉伸塑性,近来提出了异构(heterostructure)的应变硬化策略^[24-27],其微结构设计的出发点是一个力学概念,即塑性应变梯度^[28-30]。异构是有序构筑强度和塑性这2个力学性能具有显著差异的区域(例如晶粒)而形成的微结构^[24,27],其中最具代表性的是梯度结构^[13,31-35],以晶粒尺寸为梯度变量,跨尺度的晶粒在三维空间形成了从纳米晶到粗晶的梯度分布^[13,33]。梯度变量也可以

是化学组分^[36]或各种微结构和亚结构,例如相组成^[37]、孪晶^[38]和位错胞^[39]等,形成含量、体积分数或密度等的梯度分布。层状结构也是一种极具特色的异构^[24],是仅包括纳米结构和粗晶2个尺度晶粒的两级晶粒异构,最近还报道了纳米、亚微米和微米等3种尺度晶粒所构成的三级异构^[40]。其实,晶粒内部包含纳米孪晶、纳米析出^[41]以及位错胞^[42,43]等的微结构时,无论是均匀分布还是梯度分布,只要发生了特征的异质塑性变形,即在拉伸加卸载时形成了力学迟滞环^[44,45],就可称为异构。此外,还设计出了不同类型的复合异构,例如晶粒尺寸与晶粒内部纳米孪晶密度的双梯度异构^[38],以及晶粒尺寸与纳米析出相密度的双梯度异构^[46]。

异构在2个方面不同于传统的均质微结构(homogeneous microstructure),一是晶界的塑性协调变形^[26,47-51],二是基于几何必需位错(geometrically necessary dislocations, GNDs)的异质塑性变形^[26,27,44]。例如跨尺度异构中,相邻晶粒塑性变形不兼容并在三维空间相互约束,在晶界附近引起了应变梯度^[33,52],并形成了协调应变梯度的几何必需位错^[27,28,53],因而,应变梯度是异构晶界标志性的塑性响应,几何必需位错则是协调应变梯度的必然结果^[28]。研究表明,在拉伸加卸载过程中出现的力学迟滞环^[54,55],是几何必需位错较大程度地参与塑性变形并形成背应力的标志性应力应变响应^[44]。一般地,位错塑性变形机制应该能够同时解释拉伸加载与卸载过程的力学行为^[44],而单一的林位错塑性则无法解释迟滞环的形成及卸载塑性行为。换言之,力学迟滞环是异构区别于传统均质结构的关键力学塑性响应,表明异构同时具有林位错塑性以及几何必需位错的塑性行为。特别地,GNDs引起了异质变形诱导的应力,包括背应力和前应力^[42,43,56-58],引起了额外的强化^[59]、特别是额外的应变硬化^[33],后者往往与林硬化相当、甚至占比更大^[24,40],这是异构应变硬化的关键特点,也是异构提升拉伸塑性和韧性的根本原因。

研究表明异构策略可适用于金属结构材料,包

括钢铁、钛合金、铝合金、镁合金,以及中熵与高熵合金等。利用异质变形诱导的额外应变硬化,异构提高了拉伸均匀塑性以及强度与拉伸塑性之间的协同关系^[27,48,50,60-62]。同时,异构还可提升断裂韧性^[63-67]、抗疲劳裂纹扩展^[68-70]、热稳定性^[71]和抗摩擦磨损性能^[72]等。本文简要综述了异构在微观结构、塑性变形、应变硬化以及力学性能等方面的研究进展。

1 异构的微结构特征

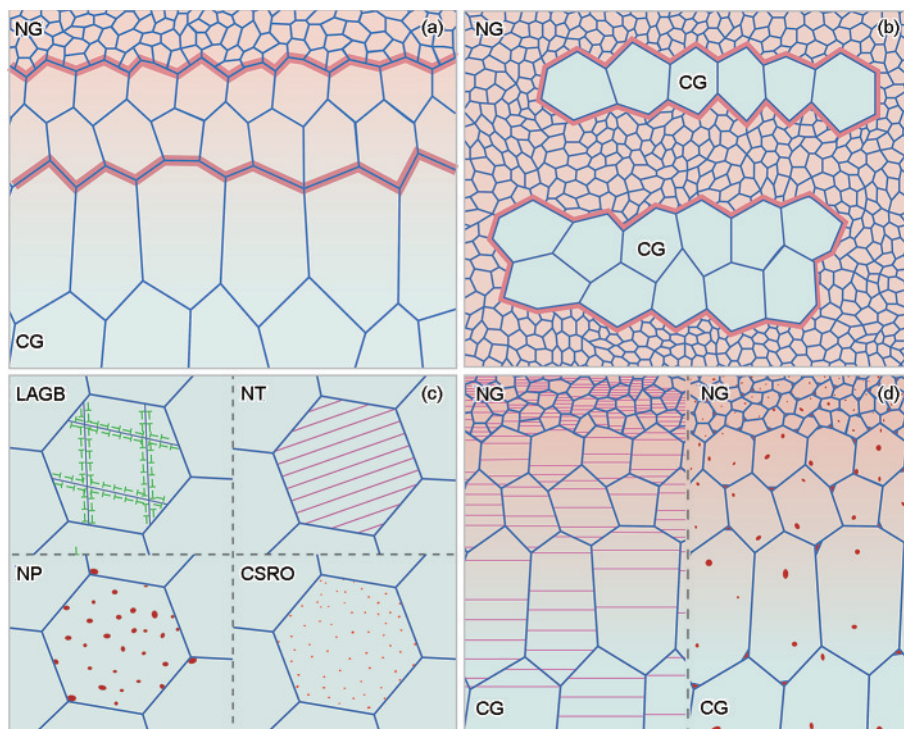
1.1 异构及其类型

异构可分为3类:一是基元异构,例如跨尺度晶粒的有序构筑以及双相结构等;二是亚基元异构,即基元内部包含了次级的组成物或亚结构,例如纳米孪晶、纳米析出或第二相,甚至小角位错界面等;三是前2种异构组合的复合异构。图1a和b是2种典型的基元异构,根据基元序构(有序构筑)的方式又可称之为梯度结构^[13]和层状结构^[24],前者的晶粒从纳米晶(NG)到粗晶(CG)在三维空间连续分布,后者则是粗晶聚集为层状并非连续地分布在高强结构的基体上。基

元异构有2个典型的微结构特征:一是跨尺度的晶粒;二是长程的异质界面(暗红色线段),异质界面两侧晶粒大的尺寸差异导致不兼容塑性,将产生几何必需位错^[28-30]。图1c示意了几种亚基元异构,晶粒内部包含各种“人工的”亚基元组成物,例如小角位错界面^[42,43]、纳米孪晶^[73,74]及纳米析出^[75-77],以及“天然的”亚基元组成物,例如中/高熵合金中纳米尺度的化学短程与中程有序^[78-80],后者往往是塑性稳定的有序结构并具有类似纳米析出阻碍位错滑移的作用^[78,81]。图1d示意了2种复合异构,即晶粒尺寸和纳米孪晶(左)/纳米析出相密度(右)的双梯度异构。

1.2 异构的基元与序构

针对异构中强度与不兼容塑性变形等力学性质差异显著的区域,提炼出塑性变形和应变硬化等具有共性特征的一个微观组成单元^[26],定义为基元,如图2所示。基元是一个组织结构相对均匀的三维区域,基元本身是一个强韧组合,例如可以是粗晶和纳米晶粒的组合,也可以是双/多相晶粒的组合。基元中含有纳米孪晶、纳米析出、第二相以及位错界等次



Color online

图1 金属结构材料的异构:基元异构(分别为梯度结构和层状结构)、亚基元异构及复合异构

Fig.1 Heterostructures (HSs) in metallic materials

- (a, b) zone HSs. Typical examples are gradient structure (a) and lamellar structure (b) (Thick dull-red lines: hetero-zone boundaries; NG: nano-grain; CG: coarse grain)
- (c) sub-zone HSs of four kinds, respectively, with the low-angle grain boundary (LAGB), nano-twin (NT), nano-precipitate (NP), and chemical short-range order (CSRO) inside the grain interior, all independently as the sub-constituent of HSs
- (d) composite-like HSs, usually with dual-gradients in both grain size and nano-twin (left)/nano-precipitate (right)

级结构或亚结构时,则共同构建为一个亚基元异构。

异构基元在微结构和力学性质上表现出几个特点。首先,基元异构中相邻区域,即2个晶粒之间存在明显、甚至跨尺度的尺寸差异(图1a和b),相应地,2个晶粒具有两极分化的力学性质组合(图2),例如粗晶的低强度大塑性与纳米晶的高强度低塑性^[13,24],尤其是明显差异的微观塑性变形和应变硬化能力。其次,基元界面称为异质区界面(hetero-zone boundary, HB)^[26],由于异质界面两侧晶粒的微观塑性不兼容^[27,48],界面的关键作用是实现相邻晶粒的塑性协调以及应变硬化,特别是针对高强纳米结构的应变硬化、抑制其早期局域化失稳^[24,26]。第三,拉伸塑性(ε_p)和应变梯度(λ)具有晶粒尺度效应(图2)^[28,29],最大的应变梯度和最强的林硬化是在微米量级的晶粒尺度范围^[20,52],这也是异构设计时选择基元中粗晶的理想晶粒尺度范围^[24]。为了描述异质界面的强度匹配与塑性协调,定义参数 ξ 为基元中强弱区域的屈服强度

比值,见式(1)。对于均质结构, $\xi \approx 1$;对于异构, $\xi > 1$ 。 ξ 用于设计并定量表征异构中基元的序构强度比,高的 ξ 值是异构基元的特征属性, ξ 决定了塑性变形时应变梯度的大小和几何必需位错的密度。

$$\xi = \sigma_h / \sigma_l \quad (1)$$

式中, σ_h 与 σ_l 分别为高强度与低强度区域的屈服强度。

异构是基元进行有序构筑而形成的,基元的序构方式决定了异构的微观塑性变形和宏观力学性能。例如,梯度异构是晶粒尺寸以连续变化的方式进行排列(图1a),基元的序构协调程度 ξ 小、但 ξ 的累积程度大;层状异构则是跨尺度晶粒的基元(图1b),序构程度很大,例如钛层状异构的 $\xi \approx 4$ ^[24]。理论分析和有限元模拟研究^[82]表明,采用最优的梯度晶粒尺寸分布,即序构,可获得与粗晶一致的拉伸塑性,与实验结果^[13]吻合。相比传统等轴状的晶粒,基元中晶粒构筑为一定长宽比的片层形态时(图1b),可更为有效地提高塑性变形和应变硬化能力^[83]。

2 异构的塑性变形

2.1 异构基元的特征力学响应

异构基元塑性变形时发生基于林位错的塑性变形,可用统计储存位错(statistically stored dislocations, SSDs)来描述林位错行为^[84]。同时,相邻的强韧微区之间塑性不协调,在异质界面及其附近形成应变梯度^[28,85],如图3a^[27,52]和式(2)所示:

$$\lambda = \frac{\partial \gamma}{\partial x} \Big|_{HB} \quad (2)$$

式中, γ 为剪应变, x 为HB的距离。

为了协调应变梯度,在界面附近形成了几何必需位错^[26,33,52,53]。因而,基元同时包括了晶粒内部SSDs与异质界面GNDs等2类位错的塑性行为^[47,50],见式(3):

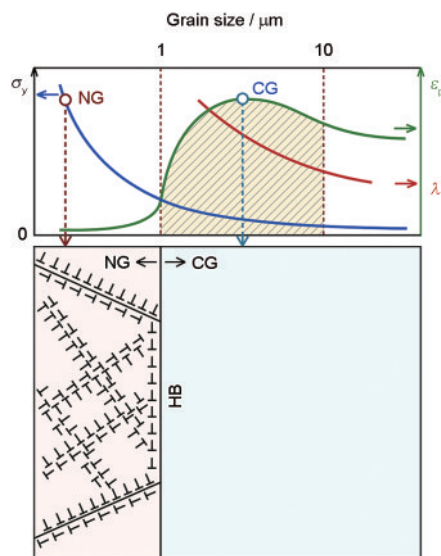
$$\rho_{total} = \rho_{SSDs} + \rho_{GNDs} \quad (3)$$

式中, ρ_{total} 为位错的总密度, ρ_{SSDs} 和 ρ_{GNDs} 分别为SSDs和GNDs的密度。为此,异构塑性变形时的应变硬化,即流变应力的增量 $\Delta\sigma$ 取决于SSDs和GNDs 2类位错,见式(4)。

$$\Delta\sigma = M\alpha\mu b \sqrt{\rho_{SSDs} + \rho_{GNDs}} \quad (4)$$

式中, M 为Taylor因子, α 为材料相关的常数, μ 为剪切模量, b 为Burgers矢量模。

一般地, ξ 越大,表明相邻晶粒的塑性不兼容程度越大,则异质界面的应变梯度就越大, ρ_{GNDs} 越高,相应地,基于GNDs的异质塑性变形以及基于GNDs的额外应变硬化占比也越大^[24,27,40]。进而,只要发生



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图2 异构基元及其微观设计

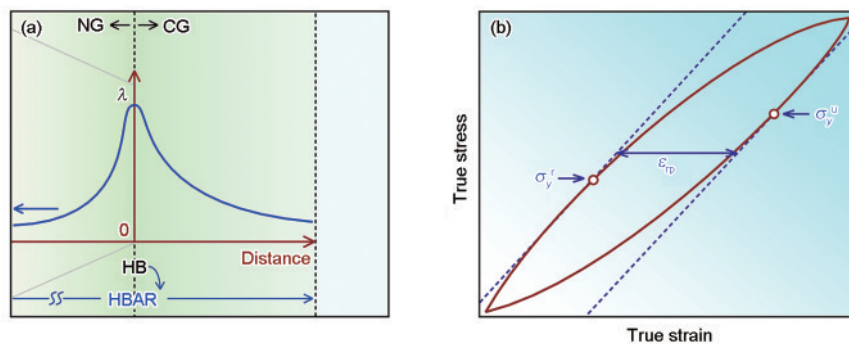
Fig.2 Schematic of characteristic zones in a hetero-structure (Upper panel: yield strength (σ_y), plastic strain (ε_p), and strain gradient (λ), all as a function of grain size. Thereinto, σ_y obeys the Hall-Petch relationship, while both ε_p and λ are of the plasticity-related size effect^[28,29]. Shadow area: the maximal strain gradient and strongest strain hardening, usually in the micron range, as the criterion for the HS design^[24,26,27]. Lower panel: characteristic HS zones, with a sharply contrasting (σ_y , ε_p) combination for the hard/soft zones. HB: hetero-zone boundary. NG here represents nano-grain of high-density dislocation tangles at/inside both the boundaries and interiors)

基于 GNDs 的异质塑性变形, 就会在拉伸卸载-再加载过程中形成力学迟滞环^[40,55], 如图 3b^[55]所示。异构在加卸载拉伸时, 应力-应变曲线上出现的力学迟滞环是其标志性的塑性变形响应^[55,61], 也是之所以称为异构的根本原因。力学迟滞环的最大宽度被定义为卸载屈服应变^[40], 一般在 0.1%~0.2%, 表明即使在外加拉伸应力状态下, 仍然发生了局域的压缩塑性变形^[40,55], 换言之, 异构在拉伸变形时发生了应力状态的改变, 局域可为多轴应力状态^[25,33], 同步辐射原位测试证实了拉伸变形时梯度结构纳米层发生了应力状态改变^[86]。实验测试和理论研究都证实了异构的 2 个标志性力学响应, 即应变梯度^[33,52,87-89]和迟滞环^[90-95]。

2.2 异质塑性变形诱导的应力

异构基元在初始塑性变形时, 异质界面附近的

局域应力会率先激活粗晶内部的位错源^[24,53], 在滑移面上发射位错, 其前端受阻于异质界面, 从而形成位错塞积^[26,27,58,96], 如图 4a 所示, 在层片异构的微米级晶粒中观察到形成的位错塞积, 如图 4b^[24]所示, 认为这些位错是几何必需位错, 其作用是协调界面塑性。随着位错塞积中位错数量的不断增加, 这些位错形成一个力, 作用于位错源并抑制其发射位错, 此时需要额外增大外加应力才能使位错源继续发射位错, 这个由于几何必需位错塞积引起、额外增加的应力被称为背应力(back stress)^[42,43,56-58], 也称为长程内应力(long-range internal stress)^[56], 作用于粗晶内部, 如图 4a 所示。同时, 位错塞积产生的这个力还作用于异质界面的另一侧, 称为前应力(forward stress)^[42,43], 其作用范围可跨越很多纳米晶粒, 这需要实验和理论模拟的进一步研究。把背应力和前应力组合起来, 称为异质变形

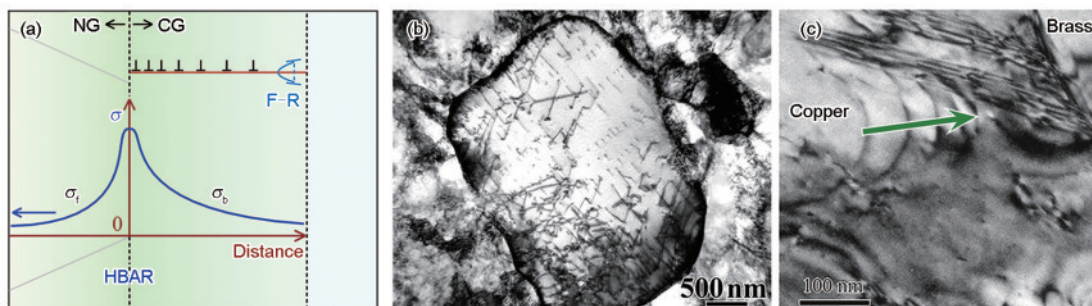


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图3 异构基元的 2 个特征力学响应: 应变梯度和力学迟滞环^[27,52,55]

Fig.3 Two characteristic mechanical responses during tensile deformation in heterostructures

- (a) distribution of λ . Upon straining, the initial HB extends to the hetero-zone boundary affected region (HBAR)^[27,52]
 (b) mechanical hysteresis loop during unload-reload cycle^[55] (σ_y^u and σ_y^r : yield stresses upon unload and reload, respectively; ϵ_{rp} (the maximal loop width): residual plastic strain)



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图4 异构背应力的几何必需位错塞积模型^[24,53]

- Fig.4 Hetero-deformation-induced stress (HDI-stress) in terms of the geometrically necessary dislocation (GND) pile-up
 (a) back stress (σ_{back}) and forward stress ($\sigma_{forward}$) exerted on CG and NG, respectively, as a function of distance inside the hetero-zone boundary affected region (HBAR). F-R: Frank-Reed source to form the dislocation pile-up on the slip plane. Blue arrow: indefinite scope of $\sigma_{forward}$ to extend into the nano-grains so far due to the lack of the experimental and theoretical evidences
 (b, c) dislocation pile-up in heterostructures^[24,53]

应力(hetero-deformation-induced stress),即 HDI-应力^[26,27]。针对晶粒内部的小角位错界面、晶界和相界等,已经建立了基于背应力的位错塞积模型^[26,42,43]。最近,透射电镜原位拉伸粗晶 Cu/纳米晶黄铜的层片异构时,观察到粗晶中位错源启动并不断向异质界面发射位错,形成了位错塞积(图 4c 中箭头所示),如图 4c^[53]所示,支持了异构背应力起源的位错塞积机制^[53]。利用拉伸加卸载测试可进行背应力的定量测试^[97],随后考虑到卸载屈服的影响进行了修正^[59],需要指出的是所计算的背应力实际上是 HDI-应力^[26,27]。

基于几何必需位错的 HDI-应力与应变硬化均取决于异构基元的序构方式。例如,基元异构中,包括梯度结构、层状结构等(图 1a 和 b),长程应变梯度引起的 HDI-应力作用范围大,而亚基元异构中 HDI-应力的作用范围则常常限制在晶粒内部(图 1c)。同时,异构基元的屈服强度差异越大,高强度纳米结构的占比越大、甚至晶粒内部的位错密度越高, HDI-应力就越大。大量的 HDI-应力测试表明,高屈服强度异构的 HDI-应力在外加应力中的占比可高达 50%~70%^[40];同时, HDI-应力随应变的增大或增加或减小,与晶粒内部位错密度和组态的演化相关^[33,40,46]。

3 异构的微结构演化

3.1 异质界面影响区

异构基元在塑性变形时,在异质界面两侧的一定范围内,发现侧向压缩应变形成了反常的负应变梯度^[52],这表明初始的异质区界面演化为异质界面影响区(hetero-zone boundary affected region, HBAR)^[27,52],如图 3^[27,52,55]所示。广义地,可以把异质界面附近形成应变梯度的区域称为 HBAR,显然,粗晶内所形成的几何必需位错主要集中在该区域。异构初始变形时,异质界面附近的局域不仅应变大,

还处于大应力的复杂应力状态,很容易激活位错源^[27,52,53],从而提高了界面附近的位错密度,这是 HBAR 负应变梯度形成的原因^[52]。进一步,推导出了层片异构 HBAR 的特征宽度 l_{HBAR} ^[52],见式(5):

$$l_{\text{HBAR}} \approx \left(\frac{\mu}{\sigma_y} \right)^2 b \quad (5)$$

计算出 l_{HBAR} 为 5~6 μm ^[52],与经典塑性应变梯度理论中材料特征长度相当^[98],也与实验测试的结果吻合。HBAR 内的负应变梯度是一个反常的应变行为,距离异质界面越近,则位错密度越高、塑性应变越大,这是几何必需位错在 HBAR 独特的位错协调行为,对 HBAR 的塑性变形和应变硬化产生关键的影响。在层片异构中^[52],HBAR 提供的额外 HDI-应力相对流变应力的占比高达约 14%,且远大于林位错提供的应力,这是导致强度与塑性匹配显著提升的原因。

3.2 异构中纳米结构的位错行为演化

纳米结构拉伸变形时应变硬化能力极低^[3,6,8,9],纳米结构进行独立的拉伸相比其在异构中进行拉伸,前者的拉伸塑性远小于后者^[13,33]。异构塑性变形的核心问题是其高强度结构的位错行为,决定了高强度结构以及异构的塑性变形和应变硬化。异构塑性变形时,纳米结构是与粗晶协调变形,从而表现出不同于其独立变形时的位错行为^[25,26]。以梯度异构中的纳米晶粒为例^[33,98],其典型特征是高密度位错缠结的晶界,如图 5a^[33]所示。在梯度结构的塑性变形初期,无论是晶界还是晶粒内部,位错从其高密度缠结中逐渐解开了缠绕,如图 5b^[33],导致位错湮灭,即位错密度降低。随后,新形成了位错并储存于晶粒内部,出现了新的位错胞和位错亚晶界,如图 5c^[33]。位错演化过程中,并没有发生界面的迁移、即晶粒长大。因而,纳米晶粒在协调变形时位错先湮灭再储存,即位错密度先降低再升高,纳米结构相应地先应

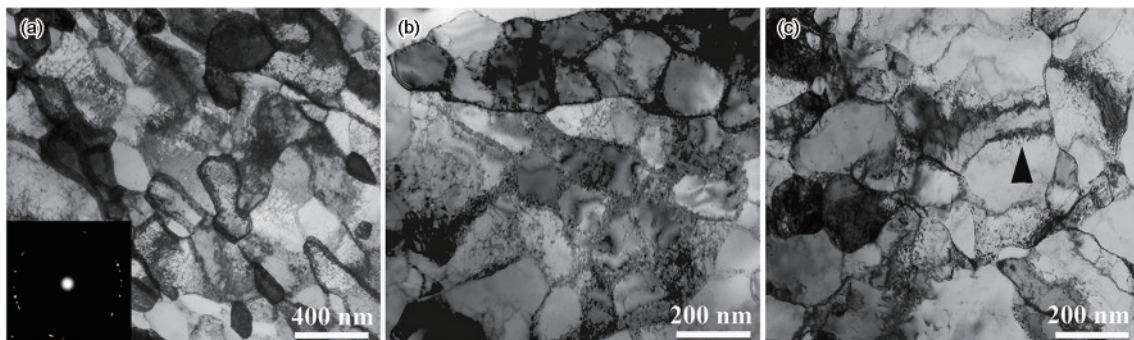


图 5 位错湮灭/形成以及位错塞积^[33]

Fig.5 Dynamic dislocation evolution in response to plastic deformation in heterostructured interstitial-free steel^[33]

(a) initially entangled dislocations of high density at/inside both the hetero-boundary and interiors

(b) dis-entanglement of dislocations (c) newly-generated dislocations

变软化而后硬化,显微硬度表现出与位错密度演化一致的变化规律^[99],即随应变的增加先降低再升高。位错演化行为很可能与作用于纳米结构的前应力有关,即前应力促使已有位错沿所在滑移面或进行反向滑移或交滑移,从而导致位错解开纠结和湮灭(disentanglement-and-annihilation)。其实,与背应力的作用类似,前应力也会改变纳米结构的局域应力状态^[33]即应变路径,大量实验和理论研究^[100,101]表明,应力状态即应变路径的改变会降低位错密度。

因而,前应力对于异构中高强度纳米结构起到了关键作用,即腾出了纳米晶粒内部的空间,使位错的重新储存成为可能,部分恢复了林位错塑性和林硬化能力,还形成了可动位错,从而减缓并抑制了纳米结构发生早期应变局域化的倾向,可进行持续的均匀变形。

4 异构塑性变形与应变硬化

4.1 异构的去应变局域化

异构中高强度晶粒中位错演化行为(图 5^[33])的直接结果是去应变局域化(strain de-localization),这是典型的塑性变形特征^[13,33]。梯度异构同样具有代表性,其纳米结构是一个独立的表层,需满足苛刻的变形要求,即与粗晶进行等塑性应变的拉伸变形。在 Cu 纳米晶粒的梯度异构中^[13],纳米 Cu 发生了变形诱导的长大,恢复了林位错塑性和林硬化。针对纳米结构很难长大的其他梯度异构以及层片异构等,利用数字图像耦合原位拉伸^[52,99]以及同步辐射原位拉伸^[86]进行定点观察并测试,发现异构中纳米结构的去应变局域化特征,即形成一条宏观应变带^[99]或多重弥散分布的微观应变带^[52,87,88]。具体地,低应变硬化的纳米结构率先发生应变局域化,即形成应变带,甚至在应变带形核初期就引起了局部颈缩^[99],应变带随后连续扩展,其前端产生了应变梯度并发生了应力状态改变^[86],促进了几何必需位错和林位错密度的不断增加^[99],同时受到塑性稳定的粗晶所约束,抑制了变形带与局部颈缩的快速扩展和早期失稳,即发生了去应变局域化。应变带扩展过程中,应变带本身承担了占比很大的塑性应变^[99];同时,在应变带扩展结束后,纳米结构还部分恢复了林位错塑性和林硬化,异构可以进行均匀变形,这是异构微观塑性变形的普适机理。

4.2 异构的应变硬化

异构塑性变形时,产生了 2 类位错,即 SSDs 和 GNDs,相应地,分别贡献林硬化与 HDI-硬化^[23]。对于均质结构,林硬化在应变硬化率(Θ_{homo})中起主导作用,见式(6),粗晶的应变硬化率缓慢降低,而纳米

结构的则快速降低,如图 6 所示。异构的应变硬化率(Θ_{hetero})包括林位错引起的林硬化、纳米结构的应变软化,以及几何必需位错引起的额外 HDI-硬化,见式(7),其中, HDI-硬化包括纳米结构和粗晶的 HDI-硬化,见式(8)。对于各种复合异构,孪晶界(TB)、相界(PB)、位错界面(DB)以及析出/第二相等都会引起额外 HDI-硬化,见式(9)。

$$\Theta_{\text{homo}} = \left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{forest}} \quad (6)$$

式中, σ 和 ε 分别为真应力与真应变,方程右边为林位错硬化。

$$\Theta_{\text{hetero}} = \left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{forest}} - \left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{SSDs}}^{\text{NS}} + \left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{HDI}} \quad (7)$$

式中,方程右边第二项为纳米结构的初始应变软化,第三项为异构的额外 HDI-硬化。

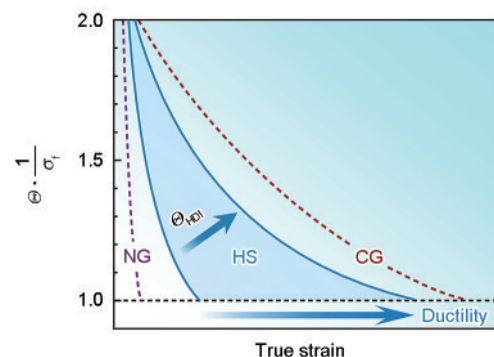
$$\left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{HDI}} = \Sigma \left[\left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{GNDs}}^{\text{NS}} + \left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{GNDs}}^{\text{CG}} \right] \quad (8)$$

式中,等号右边分别为纳米晶和粗晶的额外应变硬化。

$$\left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{HDI}} = \Sigma \left[\left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{GNDs}}^{\text{GB}} + \left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{GNDs}}^{\text{TB}} + \left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{GNDs}}^{\text{DB}} + \left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\text{GNDs}}^{\text{particle}} + \dots \right] \quad (9)$$

式中,等号右边分别为晶界(GB)、孪晶界(TB)、位错界面(DB)、析出和第二相(particle)的额外应变硬化。基于实验结果,图 6 示意了异构 Θ_{hetero} 的变化趋势,由于额外硬化的效应,异构的应变硬化率逐渐接近粗晶的,这是异构提升强度与拉伸塑性匹配的原因。

额外 HDI-硬化是异构应变硬化的本征特性。首先,前应力引起了纳米结构的额外硬化(但伴随初



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图 6 异构的应变硬化率

Fig.6 Normalized strain hardening rate ($\Theta = \frac{\partial \sigma}{\partial \varepsilon}$) by flow stress (σ_f) vs true strain (Dash horizontal line: the onset of diffuse necking according to the Considère criterion)

期的应变软化), 不仅抑制其早期塑性失稳, 还部分恢复了林位错塑性和林硬化, 使其均匀塑性应变。其次, 应变梯度具有尺度效应(图2)^[96,102,103], 在微米尺度最大^[96], 多见于1~10 μm ^[96,104], 因而, 基于几何必需位错的HDI-硬化也是晶粒尺度相关的, 粗晶在微米量级时异构的综合硬化效应最为明显^[24,103]。第三, 异构拉伸变形时, 常出现屈服降式(yield-drop-like)的非连续屈服现象^[33,55], 应变硬化率先快速下降再缓慢升高。利用引入了几何必需位错和背应力的塑性本构模型^[105,106], 发现屈服降是前应力作用于纳米结构的结果, 即纳米结构中位错密度的降低导致了瞬态软化, 随后形成新的位错并存储, 林硬化和HDI-硬化同时增加。最后, HDI-硬化的作用空间范围以及占比取决于异构中强韧匹配的序构即 ξ 值, ξ 值越大则GNDs密度越高, HDI-硬化能力也越强^[24,40]。

5 异构的额外强化

梯度异构中, 发现异构的屈服强度大于混合法则计算得到的屈服强度^[59], 或大于异构中最强组成相的屈服强度^[74], 表明异构在屈服过程中产生了额外强化。同步辐射原位拉伸结果^[86]表明, 梯度结构的屈服是从低强度粗晶到高强度纳米晶依次发生, 特别地, 在已屈服与未屈服的界面观察到一个高密度位错峰, 分析表明该位错峰对应已屈服与未屈服区域之间塑性不协调引起的几何必需位错, 这是额外强化的位错来源。针对梯度纳米孪晶Cu^[74], 微观结构观察并结合分子动力学计算模拟, 同样发现额外的强化归因于梯度结构之间相互约束而产生的大量几何必需位错的富集束, 这些位错富集束在变形初期形成, 沿着梯度方向均匀分布在晶粒内部, 富集束阻碍位错运动, 提高了强度。因而, 额外强化是异构非连续屈服导致的本征特性。

6 异构强度与塑性的协同关系

图7总结了在传统金属材料和中高熵合金中利用异构策略提升强度与塑性匹配的结果。相比均质单相金属(黄色区域), 单相的异构金属提高了拉伸均匀塑性(蓝色虚线), 即提升了强度与拉伸塑性之间的协同关系, 曲线向右上方迁移, 这归因于异构的额外应变硬化。同时, 单相fcc结构的中/高熵合金异构(红色虚线)则更为显著地提升了强度与拉伸塑性之间的协同关系, 这很可能还与其固溶强化^[107,108]、点阵畸变^[109]、化学短程有序^[78-80]和浓度波^[110]相关。特别地, 在1.5~2 GPa的超高屈服强度范围, 无论是传统合金的异构还是中/高熵合金异构, 多为依靠纳

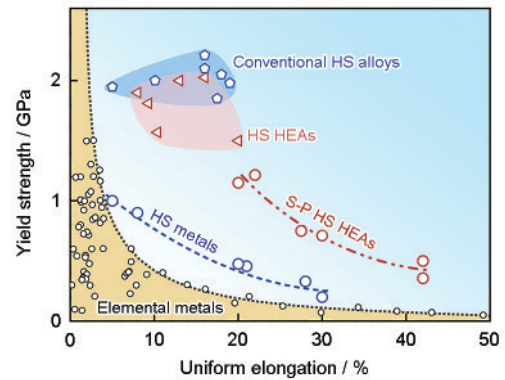


图7 异构屈服强度与拉伸均匀塑性之间的协同关系

Fig.7 Strength-and-ductility balance in metallic materials (Two areas in blue and pink: ultra-high strength (> 1.5 GPa) alloys all with the nano-structure as the matrix; HEA: high-entropy alloy; S-P: single phase)

米析出、马氏体相变和变形孪晶等的各种亚基元复合异构^[111-114], 获得了理想的均匀拉伸塑性, 二者强度与塑性的性能域也基本一致, 这表明了超高屈服强度下异构可观的应变硬化潜力。

7 展望

异构金属材料展现出了一种独特的塑性自协调力学响应, 即形成了应变梯度并因此而产生几何必需位错, 从而引起了独特的额外应变硬化, 不仅抑制了异构中高强度结构的应变局域化, 还进一步恢复了其林位错塑性和硬化并实现均匀塑性变形, 这是异构提高拉伸塑性和断裂韧性的内在原因。

利用传统的工业制备与成型技术可实现异构金属结构材料的制备。例如, 利用各种表面变形技术、扭转技术和电沉积技术等制备梯度结构, 冷轧结合退火可得到层状异构、多级晶粒异构以及各种复合异构, 利用电解沉积技术可制备孪晶片层厚度和晶粒尺寸精准可控的纳米孪晶Cu异构。同时, 通过调控热处理退火等工艺可获得不同强度级别的异构, 拓展了异构的强度与塑性匹配范围。

异构金属材料所面临的挑战在于高屈服强度的设计策略。可以预期, 异构会包括大量的纳米尺度高强度微结构, 例如析出、第二相、相变和孪生变形等, 具有先天强烈的局域化倾向, 为此, 需要在实验以及理论计算与模拟方面同时开展基于应变梯度的高密度异质界面的微观异构设计, 揭示应变梯度、几何必需位错和应变硬化的内禀相互关联, 建立纳米析出、纳米孪晶等纳米组成与额外应变硬化和林硬化的定量关联。同时, 需要对异构服役性能(例如疲劳与断裂)以及损伤容限性能的相关研究。

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