

# 表面纳米化对材料性能影响的研究进展与展望

牛赢<sup>1,2</sup>, 王壮飞<sup>1</sup>, 孙海猛<sup>1</sup>, 楚帅震<sup>1</sup>, 焦锋<sup>1</sup>

(1. 河南理工大学 机械与动力工程学院, 河南 焦作 454003;

2. 西峡县内燃机进排气管有限责任公司, 河南 南阳 474500)

**摘要:** 工程零部件失效常源于表面, 微组织结构显著影响甚至决定工程零部件服役性能, 表面纳米化技术可诱导材料微组织结构变化产生纳米晶结构表面层, 增大表层残余压应力, 对材料性能有极其重要的影响。首先综述了表面纳米化诱导微组织结构变化的过程及机理, 诱导材料产生晶粒细化、位错运动、残余压应力增大、相变等微观变化, 诱因有塑性变形、温度变化、元素渗入等。其次归纳了表面纳米化对材料性能的影响及其机理, 上述微观变化对材料疲劳强度、耐腐蚀性、摩擦磨损性能、生物学性能等产生显著影响。总结了各个典型表面纳米化工艺的特点, 相比于其他表面纳米化技术, 超声振动辅助加工具有不需引入其他元素、不污染环境、原理简单、高速高质量、成本低廉、可依托于各种传统加工工艺等优势, 对材料摩擦磨损性能、疲劳性能、生物学性能、表面浸润性和耐腐蚀性等具有积极作用。最后对表面纳米化工艺的未来发展做了展望, 其中针对性分析了超声振动辅助加工。针对纳米晶结构表面层的数字化仿真模拟极其匮乏这一现状, 将模拟仿真与试验相结合, 分析微组织结构与加工参数、微组织结构与材料性能的映射关系并建立模型直观反映尚需更全面系统的研究。材料的某些性能可能不会同时达到最优值, 依托于上述模型的综合评价体系有待建立, 纳米晶结构表面层基于相变动力学的高温稳定性等仍需深入分析探索。超声振动辅助加工技术的关键制约因素有待完善, 新材料的开发和技术手段的改进都是重要研究内容。超声振动辅助加工与其他表面纳米化方法组合使用是可探讨研究之处, 优势互补或许可进一步诱导产生更优异的材料性能。

**关键词:** 表面纳米化; 纳米晶结构表面层; 材料性能; 超声振动辅助加工

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## Research Progress and Prospect of the Effect of Surface Nanocrystallization on Material Properties

NIU Ying<sup>1,2</sup>, WANG Zhuang-fei<sup>1</sup>, SUN Hai-meng<sup>1</sup>, CHU Shuai-zhen<sup>1</sup>, JIAO Feng<sup>1</sup>

(1. School of Mechanical and Power Engineering, Henan Polytechnic University, Henan Jiaozuo 454003, China;

2. Xixia Internal Combustion Engine Intake and Exhaust Pipe Co., Ltd., Henan Nanyang 474500, China)

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作者简介: 牛赢 (1987—), 男, 博士, 讲师, 主要研究方向为精密超精密加工技术与装备。

Biography: NIU Ying (1987-), Male, Doctor, Lecturer, Research focus: precision ultra-precision machining technology and equipment.

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**ABSTRACT:** The failure of engineering parts was often caused by the surface, and the working performance of engineering parts was significantly affected or even determined by the microstructural structure. The microstructural structure of materials was induced by the surface nanocrystalline surface layer, and the residual compressive stress on the surface layer increased, and the material performance was greatly affected. According to their characteristics, surface nanocrystalline technologies could be divided into three categories: surface self-nanocrystalline (mechanical and thermodynamic methods), surface coating/deposition and hybrid nanocrystalline. Firstly, the process and mechanism of microstructural changes induced by surface nanocrystallization were reviewed. The materials were induced to produce microscopic changes such as grain refinement, dislocation movement, increase of residual compressive stress and phase transformation, which were induced by plastic deformation, temperature change and element infiltration. Secondly, the influence and mechanism of surface nanocrystallization on material properties were summarized, and the fatigue strength, corrosion resistance, friction and wear properties and biological properties of materials were significantly affected by the above microscopic changes. The application, advantages and limitations of cold rolling, laser shock peening, shot peening, high pressure torsion, supersonic fine particles bombarding, surface coating/deposition and equal channel angular extrusion were summarized. Compared to other surface nano technology, ultrasonic vibration assisted treatment had no need to introduce other elements, no pollution, simple principle, high speed and high quality, low cost, could be on various advantages of the traditional processing technology, it had a positive effect on the friction and wear properties, fatigue properties, biological properties, surface wettability and corrosion resistance of materials. Finally, the future development of surface nanocrystalline technology was prospected, and the ultrasonic vibration assisted processing was analyzed. Digital simulation of the surface layer of nanocrystalline structure was extremely scarce. It needed more comprehensive and systematic research to combine simulation and experiment, analyze the mapping relationship between microstructure and processing parameters, microstructure and material properties, and establish a model for direct reflection. Some properties of the materials might be difficult to reach the optimal value at the same time, an evaluation system based on the above model needed to be established in order to improve the comprehensive properties of materials. The mechanism of nanocrystalline surface layer improving material properties was limited by existing observation methods and processing technology, the mechanism of surface nanocrystalline surface layer induced by surface nanocrystalline surface layer and high temperature stability based on phase transformation dynamics still need to be further analyzed and explored. The key of ultrasonic vibration assisted machining technology included ultrasonic vibration unit, ultrasonic cutting tool, ultrasonic cutting machine tool, ultrasonic system, CNC machine tool integration technology, etc. These key restricting factors needed to be improved, the development of new materials and the improvement of technical means were important research contents. Surface nanocrystalline methods generally affected only relatively shallow layers of materials, the improvement of the overall properties of the material was restricted. The combination of ultrasonic vibration-assisted machining with other surface nanocrystallization methods was an area that could be explored, and complementary advantages might further induce better material properties.

**KEY WORDS:** surface nanocrystallization; nanocrystalline surface layer; material properties; ultrasonic vibration assisted machining

磨损、疲劳和腐蚀是工程零部件失效的主要原因,常始于材料表面,与表层组织性能关系密切,优化表层组织性能对综合材料性能的提高尤为重要。1999年卢柯等<sup>[1]</sup>提出表面纳米化的概念,在不改变基体状态条件下诱导材料产生纳米晶结构表面层,从而大幅改善材料性能,为结构材料的突破提供新思路。相比于粗晶材料,纳米晶材料常具有更优越的材料性能,表面纳米化作为提高材料性能的典型有效途径而被广泛应用。

将表面纳米化技术根据特点不同分为三类:表面自纳米化(机械法和热力学法)、表面涂层/沉积和混合纳米化。其中表面自纳米化<sup>[2]</sup>仅通过材料自身产生

改变而不另外引入成分,并可依托于传统加工工艺,应用价值较高,对该部分进行了重点综述。

表面纳米化常诱导材料产生晶粒细化<sup>[3-4]</sup>、位错运动<sup>[5]</sup>、相变<sup>[6]</sup>等微观变化,诱因有塑性变形、温度变化、元素渗入等,这些微观变化对材料疲劳性能、耐腐蚀性能、摩擦磨损性能、生物学性能等产生显著影响。相比于其他表面纳米化技术,超声振动辅助加工具有不需引入其他元素、不污染环境、原理简单、高速高质量、成本低廉、可依托于各种传统加工工艺等优势,对材料摩擦磨损性能<sup>[7]</sup>、疲劳性能<sup>[8]</sup>、生物学性能<sup>[9]</sup>、表面浸润性<sup>[10]</sup>和耐腐蚀性<sup>[11-12]</sup>等具有积极作用。

首先综述了表面纳米化工艺对晶粒、位错和金相等的影响及其机理, 其次总结了表面纳米化对材料性能的影响及其机理, 之后阐述了超声振动辅助加工技术对材料性能的影响机理, 最后对表面纳米化工艺的未来发展做了展望, 其中针对性分析了超声振动辅助加工技术。

## 1 表面纳米化对材料微观组织的影响

### 1.1 表面纳米化对晶粒的影响

晶粒的常见变化有晶粒细化、晶粒拉伸、晶粒取向/角度转变等, 纳米晶材料常具备比粗晶材料更优的材料性能, 研究表面纳米化对晶粒的影响及机理利于进一步提高材料性能。

晶粒细化通常多途径同时发生, Lu 等<sup>[13]</sup>采用激光冲击强化处理工业纯钛, 晶粒细化分为 2 种途径, 如图 1 所示: (1) 微孪晶-微孪晶亚微米尺度多向交错。该过程中微孪晶占主导地位, 原始粗晶受冲击后被平行微孪晶分割成数十纳米宽双基体片层(图 1a), 多次激光冲击后双基体片层被第二方向平行微孪晶切割成三角形、菱形亚晶块(图 1b), 继续激光冲击后, 第三方向的平行微孪晶将粗晶粒细化至微米级, 形成等轴细晶。(2) 微孪晶-位错壁纳米尺度二次交错。该过程中位错占主导地位, 微米级薄板条结构被次级微孪晶纵向分解为纳米级双基体片层(图 1c), 位错聚集成竹节状横向位错壁, 将双基体片层横向击穿为等轴亚结构(图 1d), 应变继续增加, 大角度

晶界出现, 晶粒细化至纳米级。

变形和相变都可能诱导高密度位错产生, 位错重排产生大角度晶界致使晶粒细化, 该过程与应变率、温升密切相关。Hossain 等<sup>[14]</sup>研究发现静态压缩低合金高碳钢过程中产热少、材料应变率较低, 位错角逐渐增大产生新晶界但不足以发生再结晶, 而施加冲击时应变率高、产热多、温升快, 致使位错角迅速增大并导致爆炸性再结晶。申宏卓等<sup>[15]</sup>通过波纹辊轧制方法处理 Mg/Al 复合板, 等效应变和塑性变形热的产生促进了变形晶粒动态再结晶, 变形区微组织主要为等轴晶、孪晶和动态再结晶晶粒。

经过表面涂层/沉积处理可在原始基体表面直接生成新的细晶层。王建升等<sup>[16]</sup>在铸钢表面通过电火花沉积技术制备出 WC-4Co 沉积涂层, 在涂层中下部和过渡区之间的区域中晶粒尺寸达到纳米级, 这些超细颗粒呈弥散形式。Walunj 等<sup>[17]</sup>研究了添加 Zn/Co 元素对电沉积 Ni-B 镀层的影响, 发现 Zn/Co 元素在基体中均匀分散, 基体形核位置增加抑制了晶粒生长, 镀层基体结晶度改善, 相比于原始镀层晶粒更加细化。

Lan 等<sup>[18]</sup>冷轧处理 TNZSO 合金发现随轧制量增加, 表层晶粒逐渐伸长为纤维条状, 晶格畸变量增大, 孪晶在位错滑移作用下破碎为纳米晶, 亚晶粒尺寸减小。Saeed 等<sup>[19]</sup>采用表面机械研磨工艺处理工业纯钛产生晶粒细化层, 厚度随处理时间的增加而增大, 加工硬化效应使得塑性变形能量更难向深处传递, 晶粒细化层厚度增大速率逐渐减小, 厚度存在极限值, 孪晶长度随处理时间的增加而减小。

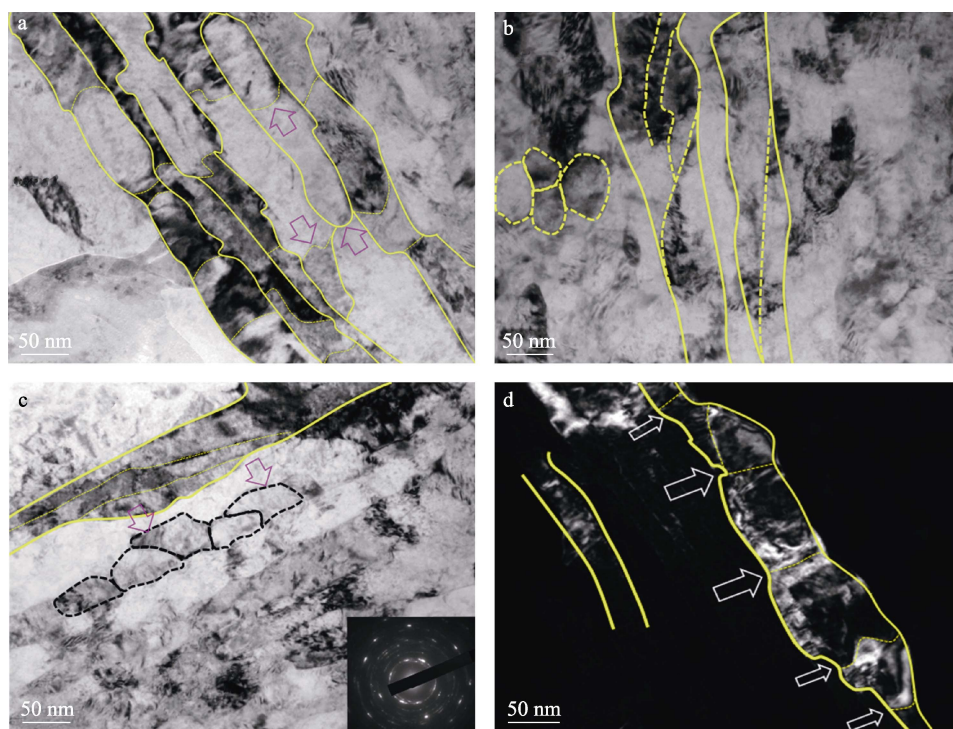


图 1 晶粒细化过程中的微观形态<sup>[15]</sup>

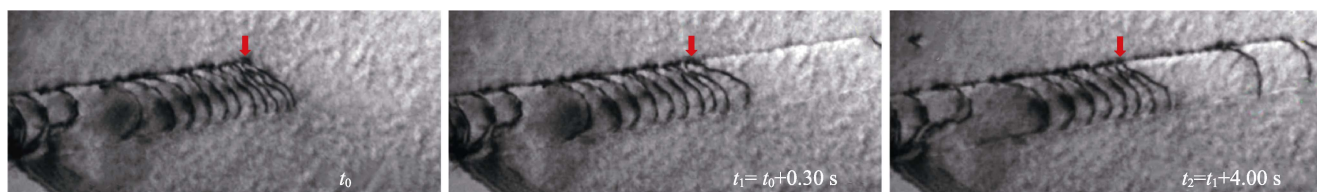
Fig.1 Micromorphology during grain refinement<sup>[15]</sup>

## 1.2 表面纳米化对位错的影响

位错运动对晶粒细化具有推动作用,高密度位错为再结晶提供驱动力。高密度位错层可抑制疲劳裂纹产生,位错扩散层可减缓疲劳裂纹扩展速度<sup>[20]</sup>。表面纳米化常诱发位错运动,位错运动剧烈程度通常与材料变形量呈正比,对位错的影响主要有位错密度增大、位错缠结、位错滑移等形式。

表面纳米化处理诱导位错运动,位错运动受阻堆积导致密度增大。Yao 等<sup>[21]</sup>观察发现塑性变形时平面

Frank-Read 源产生位错环,应变增加位错膨胀离开源,破坏了滑移面化学秩序,位错最终到达晶界或卡在晶粒内部,滑移面位错密度逐渐增大,位错堆积导致滑移面硬化。持续的塑性变形产生新的滑移带,滑移带间距减小并导致应力增大是材料应变硬化的主要原因。Kim 等<sup>[22]</sup>研究了高锰轻量化钢的位错运动,图2为亮场透射电镜观察到的位错滑移过程,位错在晶界处产生后平面滑动,高密度位错滑移形成滑移带,位错在通过箭头处时滑移明显被推滞,将其归因于位错和 L'12 有序相的相互作用。



2 位错滑移过程<sup>[22]</sup>

Fig.2 Dislocation slip process<sup>[22]</sup>

王全龙等<sup>[23]</sup>模拟了单晶铜纳米压印过程,发现压头挤压促使材料变形,变形成能积聚导致位错形核并向内部滑移产生堆垛层错,亚表层出现 V 形位错环。Chen 等<sup>[24]</sup>采用湿喷丸法处理 Ti-6Al-4V 合金后,试样表面剧烈弹塑性变形产生大量位错,位错滑移过程中碰撞堆积导致位错缠结,形成不规则位错胞,位错滑移、孪晶-孪晶交叉等导致晶粒细化。

## 1.3 表面纳米化对金相的影响

金相指金属/合金各种成分在基体内部的物理/化学状态,不同的金相表现出不同的组织结构,如奥氏体是面心立方结构、马氏体是体心立方结构,不同金相对材料性能发挥着不同作用,如奥氏体有助于塑性、韧性提高,马氏体有助于硬度、强度提高<sup>[25]</sup>,表面纳米化诱导金相状态改变显著影响金属材料性能,不同相的体积分数受塑性变形、温度变化等影响。

Yang 等<sup>[26]</sup>建立 AZ31 镁合金模型进行分子动力学模拟,图3a表示合金经单轴压缩处理后可能的相变(Phase Transformation, PTF)形式,由原始密排

六方堆积-M 相转为偏角密排六方堆积-N 相,或因原子位置变化转变为面心立方堆积相或体心立方堆积相,过程均可逆。图3b显示原子水平方向间距增大、其他方向间距减小导致密排六方堆积相转为面心立方堆积相。

应变率影响相变过程,Hossain 等<sup>[13]</sup>通过动态冲击处理工业级高碳钢,冲击处理初期形变提供能量使奥氏体相压缩变形为马氏体相,奥氏体比例减小,应变率增大使奥氏体减少更明显。表面纳米化工艺参数影响相变趋势走向,Ding 等<sup>[6,25]</sup>磨削处理马氏体不锈钢时发现其他参数不变时,切削深度减小、工件速度降低时铁素体向奥氏体转变量减小,马氏体向奥氏体的转变量增加,砂轮转速与转变量的关系并非单一的正相关或负相关。

## 2 表面纳米化对材料性能的影响

磨损、疲劳、腐蚀等失效形式大多发生在材料表面,与材料表层微组织结构关系密切,表面纳米化诱导材料发生晶粒细化、位错运动、残余压应力增大、相变等,诱因有塑性变形、温度变化、元素渗入等,对疲劳性能、耐腐蚀性能、摩擦磨损性能、生物学性能等产生显著影响。

### 2.1 表面纳米化对疲劳性能的影响

疲劳失效是一种典型失效形式,如统计发现 90% 的航空钛合金零部件失效为疲劳失效<sup>[27]</sup>。表面纳米化诱导晶粒、位错和金相变化产生纳米晶结构表面层,增大表层残余压应力,对疲劳性能有积极影响。残余压应力受控于材料塑性变形程度,随深度增加先增大至峰值后减小至谷值,更深处因材料自平衡效应转为

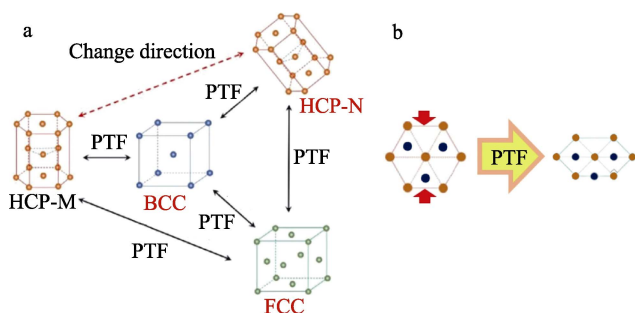


图3 AZ31 相变原理及相互转化<sup>[26]</sup>

Fig.3 AZ31 Phase transition principle and mutual transformation<sup>[26]</sup>



残余拉应力<sup>[28-29]</sup>。

Wang 等<sup>[30]</sup>采用改性表面纳米结晶技术诱导工业纯钛薄壁管状样品产生如图 4a 所示梯度纳米晶结构表面层, 近表面高密度位错胞、表面下 100  $\mu\text{m}$  片层晶粒强变形区、表面下 1 200  $\mu\text{m}$  粗晶分别如图 4b、

图 4c、图 4d 所示, 双轴拉扭疲劳试验表明经过处理的试样寿命更长。Erfan 等<sup>[31]</sup>和 Roland 等<sup>[32]</sup>分别采用喷丸和表面机械磨削处理 316L 不锈钢, 处理后材料微观组织细化产生纳米晶结构表面层, 表层塑性变形产生高残余压应力, 具有抑制疲劳裂纹萌生、扩展的作用。

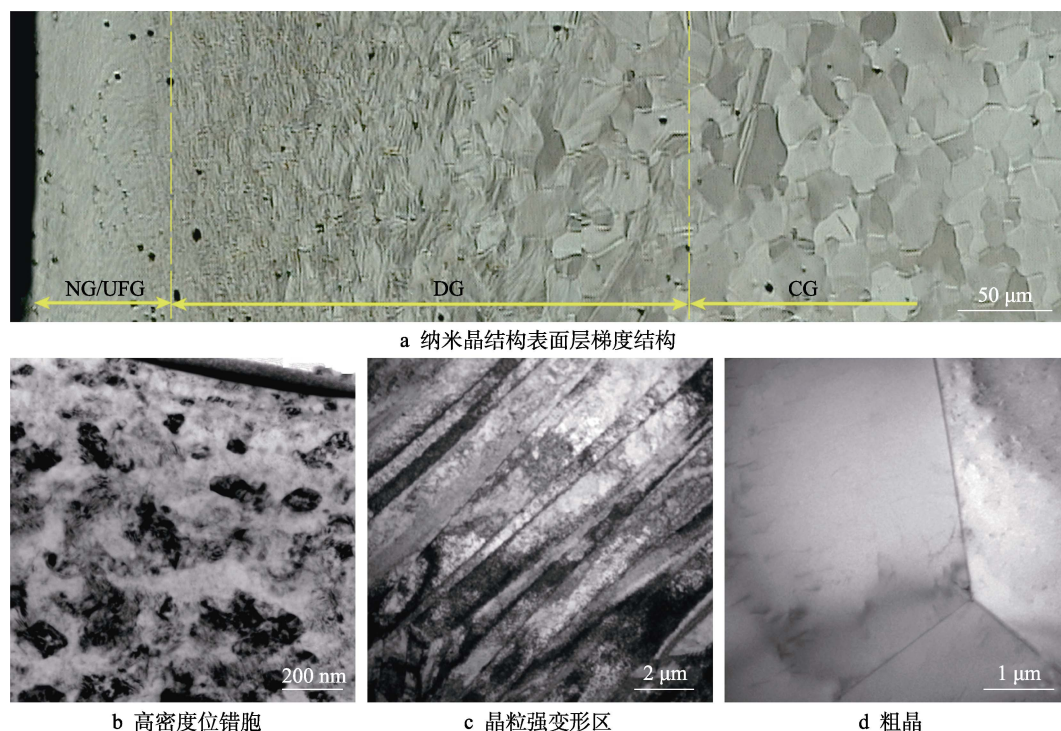


图 4 SNC 钛管状试样显微组织特征<sup>[30]</sup>

Fig.4 Microstructure characteristics of titanium SNC tubular specimens<sup>[30]</sup>

联合使用多种表面纳米化工艺可诱使材料疲劳性能进一步增强。Luo 等<sup>[33]</sup>采用激光冲击强化工艺处理钛合金后形成纳米级 (60~200 nm) 晶粒, 振动抛光引起材料高密度位错重排, 将 2 种工艺复合诱导产生了更均匀的纳米组织, 表面粗糙度更小, 相比于仅振动抛光处理, 疲劳强度从 438 MPa 提高至 544 MPa。

材料疲劳强度提高归因于: (1) 稳定、致密的纳米晶结构表面层增大了材料表层显微硬度、强度, 改善了摩擦磨损性能; (2) 近表面残余压应力增大, 抑制裂纹形核、裂纹源延伸扩展, 并对裂纹具有一定的修复作用, 残余压应力抵消掉部分外界应力, 减小材料所受应力; (3) 纳米晶结构表面层的存在使疲劳裂纹源由近表面转移至内部, 裂纹产生难度增大, 裂纹数量减少且更细小; (4) 表面质量改善缺陷减少、屈服强度提高使得金属材料抗应力集中性能增强, 不易疲劳失效。

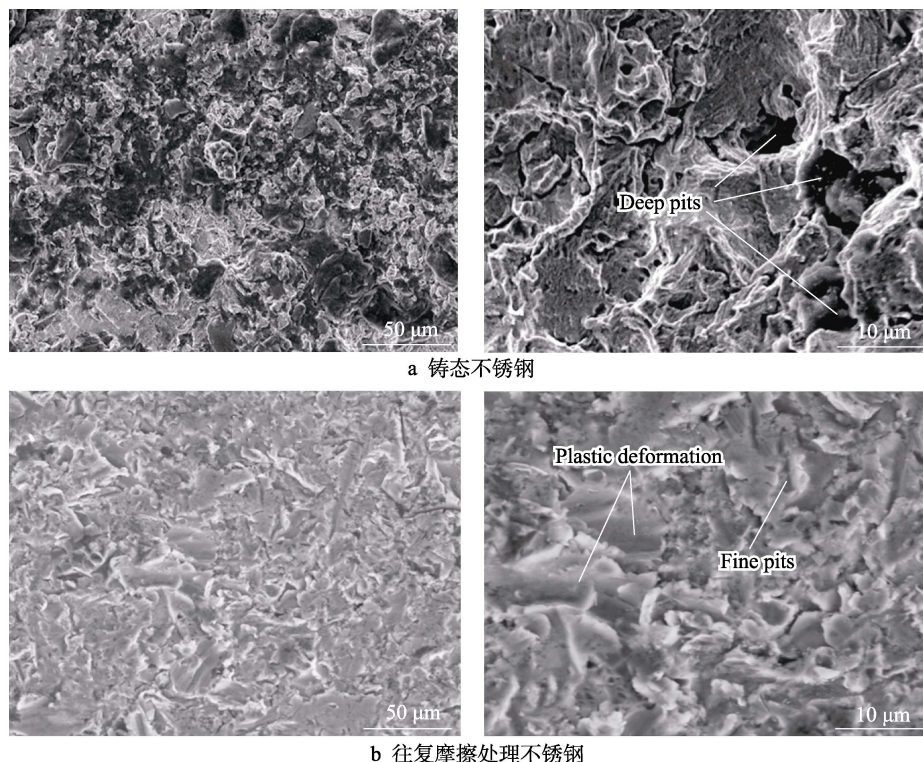
## 2.2 表面纳米化对耐腐蚀性能的影响

船舶外壳、血管支架、人造骨等零部件常接触腐蚀性液体, 采用表面纳米化方法在材料表面诱导产生纳米晶结构表面层可有效提高材料耐腐蚀性。

表面纳米化处理影响材料电化学参数。Singh 等<sup>[34]</sup>

机械研磨处理低碳钢后晶粒细化产生纳米晶结构表面层, 对腐蚀离子阻碍作用增大, 溶液与基底间界面处载流子活性增大, 材料耐腐蚀性显著提高。Arora 等<sup>[35]</sup>采用往复摩擦处理不锈钢, 表面变形产生高密度位错出现纳米晶和纳米孪晶, 材料硬度、强度提升, 转速为 388 r/min 时, 试样的极化电阻比铸态钢高 2 个数量级, 腐蚀速率由 8  $\mu\text{m}/\text{cm}^2$  降至 0.29  $\mu\text{m}/\text{cm}^2$ , 耐腐蚀性能提高。如图 5a 所示, 铸态试样腐蚀严重, 产生深腐蚀坑和条纹, 处理过的试样 (图 5b) 腐蚀坑细小, 损伤较轻。

表面纳米化处理对材料微组织的细化、强化作用提高了材料耐腐蚀性能。李宁等<sup>[36]</sup>采用剧烈塑性滚柱滚压方法处理纯铁产生最小晶粒尺寸达 300 nm 的梯度超细晶表面层, 腐蚀试验显示处理过的试样在 6%FeCl<sub>3</sub> 溶液中的腐蚀速率约为原始粗晶试样的一半, 表层晶粒尺寸大幅减小和形成强织构是其耐腐蚀性能显著增强的主要原因。Huang 等<sup>[37]</sup>采用机械研磨方法诱导 Ti-25Nb-3Mo-3Zr-2Sn 合金产生  $\beta$  相和高密度位错组成的纳米晶结构表面层, 晶粒尺寸从微米级减小至纳米级, 后退火试验显示腐蚀电流密度对晶粒尺寸变化更敏感, 晶粒细化与高密度位错相比, 其对材料耐腐蚀性能的贡献更大。

图5 铸态不锈钢和往复摩擦处理不锈钢腐蚀对比<sup>[35]</sup>Fig.5 Corrosion comparison of as-cast stainless steel (a) and reciprocating friction treated stainless steel (b)<sup>[35]</sup>

材料耐腐蚀性提高归因于：(1) 材料产生致密、稳定的纳米晶结构表面层，对基体具有钝化保护作用；(2) 对材料电化学参数的积极影响，晶粒细化、位错密度增加使得晶界处渗透率减小，基体极化电阻增大、离子释放速率降低，抑制了纳米晶体表面和游离离子间电化学反应；(3) 表面缺陷减少增大了腐蚀坑成核难度，腐蚀坑的减少缓解了表面应力集中，源于腐蚀坑的裂纹减少，缓解了向材料内部的腐蚀。

## 2.3 表面纳米化对摩擦磨损性能的影响

磨损作为工程零部件主要失效形式之一，浪费资源，拖延工作进程，甚至导致事故发生，造成巨大生命财产损失，表面纳米化处理诱导材料产生纳米晶结构表面层可显著提高材料摩擦磨损性能。

表面纳米化处理使材料微组织细化，显微硬度提高，磨损方式转变。董美伶等<sup>[38]</sup>采用超音速微粒轰击 TC4 合金产生纳米晶结构表面层，随着轰击时间增加，表面层厚度增加，晶粒尺寸减小， $\alpha'$ 相含量升高，并导致材料硬度增大，试样主要磨损方式由黏着磨损转为磨粒磨损。Deng 等<sup>[39]</sup>采用高压扭转工艺处理 Ti6Al4V，在高温高压条件下材料发生大塑性变形，微组织显著细化得到了较均匀的纳米结构，显微硬度提高约 41%，摩擦因数减小约 24%，降低了黏着磨损，处理后的试样磨损轨迹更窄，特定磨损率整体降低约 48%。Nouri 等<sup>[40]</sup>采用先渗铝后锤击的方法处理 Mg-3Al 合金，形成保护性更强的钝化膜，微组织细化并引入了硬质  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> 相，增强了镁合金摩擦磨损性能。

郭炜<sup>[41]</sup>采用反复压缩法处理 AZ31-Si 镁基复合材料，如图 6 所示，随着模锻和墩压道次的增加，基体动态再结晶平均晶粒尺寸逐渐减小、尺寸分布更均匀，Mg<sub>2</sub>Si 相弥散化，Mg<sub>2</sub>Si 由树枝状破碎为细小多角块状，SiC 纳米颗粒团簇解离并均匀分布，纳米复合材料的摩擦磨损性能提高。

张浩等<sup>[42]</sup>采用激光熔覆技术在高速钢表面制备出 Fe-Al-Ti-WC 复合涂层，发现涂层中弥散分布着 Al<sub>2</sub>O<sub>3</sub>、Al<sub>3</sub>Ti、Fe<sub>3</sub>Al、TiC 等硬相，具有细化晶粒的作用，磨损试验显示复合涂层的耐磨性比原始基体提高 3.5 倍。

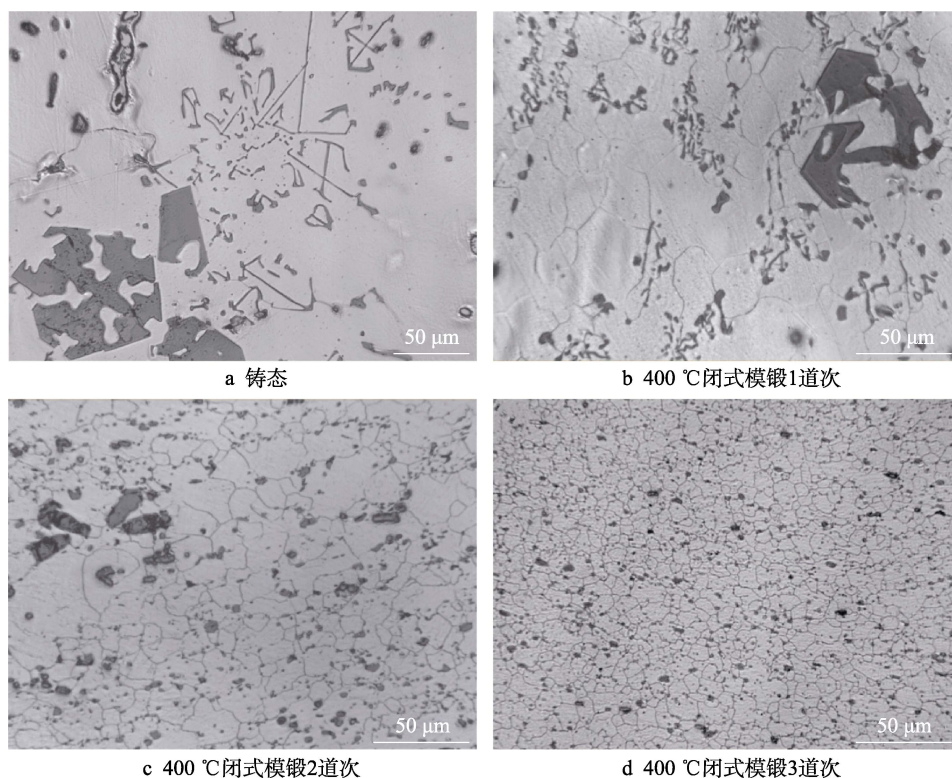
材料摩擦磨损性能提高归因于：(1) 表面质量提升使材料表面粗糙度降低、摩擦因数减小；(2) 位错密度增大、晶粒细化及硬质相的产生使材料表层致密性提高，显微硬度提升，接触面积减小，不易发生黏着磨损；(3) 纳米晶结构表面层更具保护性和附着力，起到了钝化作用，改善了摩擦磨损性能。

## 2.4 表面纳米化对生物学性能的影响

生物材料可植入人体或代替原有结构以恢复人体某部分形态或功能，表面纳米化手段可提高现有材料的生物相容性、机械性能，避免使用价格昂贵、有潜在毒性或易引起过敏的材料。

Sara 等<sup>[43]</sup>发现金属生物材料表面氧化层具有化学惰性、热力学稳定性、低血清溶解度、浸润性等特征，影响细胞分化和蛋白质吸收。大塑性变形诱发晶粒细化可调节表面氧化层状态，促进细胞黏附、扩散、存活、后期活性等行为，增强材料力学性能。



图 6 铸态及 400 °C 闭式模锻处理的镁基复合材料组织面<sup>[41]</sup>Fig.6 Microstructure of magnesium matrix composites as cast (a) and closed die forging at 400 °C (b)<sup>[41]</sup>

表层纳米纤维形态影响生物相容性。Hajizadeh 等<sup>[44]</sup>采用等通道转角挤压法制造了纳米晶医用 316L 不锈钢, 研究分析了纳米晶样品和粗晶样品的生物学行为, 细胞培养试验显示, 纳米晶样品与培养基界面处细胞增殖更强。Estrin 等<sup>[45]</sup>发现商用纯钛经等径角挤压后达到超细结晶度, 平均晶粒尺寸从 4.5  $\mu\text{m}$  减小至 200 nm, 细胞培养试验显示晶粒细化显著促进了成骨前细胞增殖, 更利于骨组织生长。Lu 等<sup>[46]</sup>使用滑动摩擦处理工艺诱导工业钛片产生纳米晶结构表层, 钛片耐腐蚀性能增强。如图 7 所示, 细晶钛片 (图 7b) 相比于粗晶钛片 (图 7a) 表现出更高的生物相容性, 显著改善了细胞附着、增殖状况。Raducanu 等<sup>[47]</sup>发现 Ti-Zr-Ta-Nb 合金经累积滚压焊处理后杨氏模量由 58 GPa 降至 46 GPa, 更接近天然皮质骨, 合金主要电化学参数改善, 相比于铸态合金, 极化电阻更高、离子释放速率更低, 试样耐腐蚀性增强, 更适宜用作骨替代材料。

生物学性能提高归因于: (1) 纳米晶结构表面层的形成在 2 个方面 (直接: 表面层的钝化隔绝作用; 间接: 抑制了电化学反应) 提高了材料在体液环境下的耐腐蚀性; (2) 纳米晶结构表层表现出微纹理, 细胞更易附着增殖, 生物相容性提高; (3) 表面硬度、耐磨性等力学性能提高, 更宜用作骨质材料等。

诱导材料表面产生晶粒细化、位错密度增加、相变、位错堆积等微组织变化也导致材料的塑性变形能

力<sup>[48]</sup>、屈服强度<sup>[49-51]</sup>等得到提高。

表面纳米化诱导材料产生纳米晶结构表层对疲劳强度、耐腐蚀性能、摩擦磨损性能和生物学性能等的提高有积极作用, 但仍存在一些问题: (1) 表面纳米化对材料性能的定性影响基本达成共识, 但受限于现有观测技术, 微组织的转变和强化机制仍缺乏全面系统的研究; (2) 实际工况相比于实验室更为苛刻复杂, 表面纳米化技术在工程实际的应用还需进一步研究; (3) 表面纳米化引起微组织变化进而影响材料性能, 其间并非单一的正/负相关关系, 而是在一定条件下具有最优解, 对不同因变量的影响甚至截然相反, 分析加工参数、微组织、材料性能间的映射关系并建立模型, 并做出评价体系使得综合材料性能最佳是重要任务; (4) 位错密度增大、晶粒细化、相变往往相伴发生, 其间关联及各自对材料性能的影响有待更深入研究; (5) 生产中常需对材料进行退火处理等, 影响纳米晶结构表层的热稳定性, 对表层基于相变动力学的高温稳定性仍需细致研究。

经表面纳米化处理后材料的晶粒、位错、金相等发生变化, 并对材料的疲劳性能、耐腐蚀性能、摩擦磨损性能和生物学性能等产生影响。不同的表面纳米化方法具有不同的加工特性, 在适用场合、成本、加工质量、加工效率、是否环境友好等方面存在较大差异。因此, 表 1 总结了几种常用表面纳米化方法的适用场合、应用优势和局限性等内容。

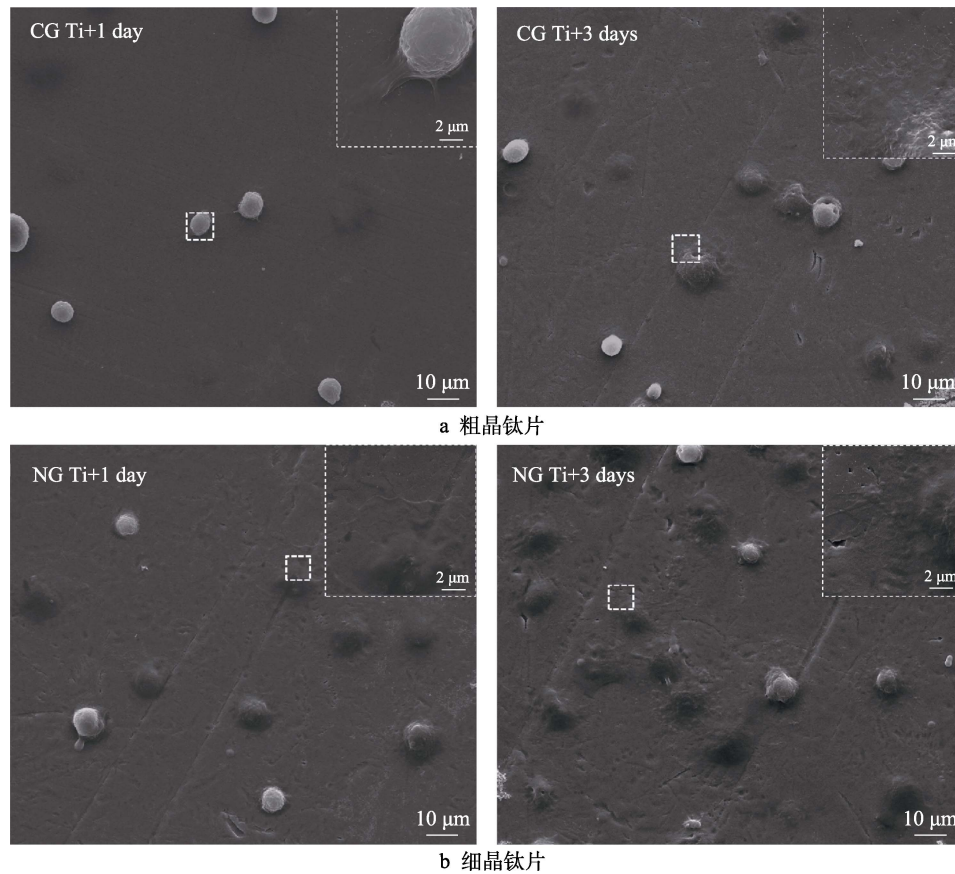


图 7 粗晶钛片与细晶钛片培养不同时间细胞增殖状况对比<sup>[46]</sup>  
Fig.7 Comparison of cell proliferation between coarse (a) and fine (b) crystal titanium slices cultured at different time<sup>[46]</sup>

表 1 常用表面纳米化方法对比

Tab.1 Comparison of common surface nanocrystalline methods

| Processing method                    | Commonly used/<br>applied occasion                                  | Application advantages   | Limitations   |
|--------------------------------------|---|--|---|
| Cold rolling                         | Homogeneous continuous rigid-plastic body                           | Good surface quality, high speed, high output, make it a variety of cross section form   | More complicated process, suitable for simple deformation of parts, size error and work hardening phenomenon, weaker local concentrated load capacity     |
| Laser shock peening                  | Large, complex curved surface, the structure of the mems components | High energy, high pressure, high strain rate, without mechanical and thermal stress damage, deep impact layer, good surface quality, no pollution, non-contact         | More complex optical system, expensive equipment cost, more complicated pretreatment process, more auxiliary device                                       |
| Shot peening                         | Has a certain thickness, size and shape require low precision       | Equipment structure is relatively simple, low cost, low maintenance cost, less wearing parts, not restricted by the shape and location, convenient operation, flexible | Lower unit production, must match the high-power air compressor station, larger energy dissipation  |
| High pressure torsion                | Small materials   | Deformation is uniform, low deformation resistance, large deformation  | Suitable for handling samples of small volume, difficult to mass production, uniformity of sample affected by the process and raw material microstructure |
| Supersonic fine particles bombarding | Large area of complex shape structure                               | Particles can be recovery, low cost, no pollution, high efficiency, simple operation safety  | Resulting in the loss of the sample material, the change of surface topography and surface roughness increased  |



续表 1

| Processing method              | Commonly used/<br>applied occasion     | Application advantages   | Limitations  |
|--------------------------------|--|--|--|
| Surface coating/deposition     | Has a wide range, large area materials | Can coating on substrate material and complementary advantages, is relatively easy and flexible, high productivity and coating material widely | Uneven distribution of coating/sediment layers, poor surface quality of sample   |
| Equal channel angular pressing | Larger size of bulk materials          | Will not change material area and the cross section shape, low working pressure, low pressure large deformation                                | Extrusion force is relatively complex, the stress distribution channel, channel stress concentration around the corner, larger internal pressure |

3 超声辅助表面纳米化对材料性能的影响

表面纳米化工艺可通过表面自纳米化(机械法和热力学法)、表面涂层/沉积和混合纳米化等途径实现金属材料纳米晶结构表面层的构建。相比于其他表面纳米化技术,超声振动辅助加工具有不需引入其他元素、不污染环境、原理简单、成本低廉、可依托于各种传统加工工艺等优势,超声辅助表面纳米化具有比冷轧法更简便、易操作的流程,可达到比超音速微粒轰击法、表面涂层/沉积法更优的表面质量等。适用于硬脆性等难加工材料,对表面质量<sup>[52-55]</sup>、硬度<sup>[56-58]</sup>、强度<sup>[57]</sup>和屈服强度等有积极作用,这里着重综述对摩擦磨损性能、疲劳性能、生物学性能、表面浸润性和耐腐蚀性能的影响。图 8 为普通磨削与超声辅助磨削<sup>[53]</sup>加工 SiCf/SiC 复合材料槽壁质量对比,后者槽壁毛刺、崩边等缺陷减少表面质量显著改善。

3.1 超声辅助表面纳米化对摩擦磨损性能的影响

超声振动辅助加工可诱导材料产生纳米晶结构表面层,增大表层残余压应力,在材料表面制备出微结构<sup>[59]</sup>,提高材料摩擦磨损性能。

Amanov 等<sup>[60]</sup>发现 AZ91D 镁合金经超声纳米晶表面改性技术 (Ultrasonic Nanocrystalline Surface Modification, UNSM) 处理后,表面粗糙度减小、磨损率降低,其中硬度最高的 UNSM-III 磨痕最窄,如图 9 所示。原始试样氧化层较厚,滑动过程中常混入变形的表面材料,超声纳米晶表面改性处理可抑制氧化层形成,改善材料摩擦磨损性能。亦有研究表明超声振动辅助加工在材料表面诱导产生鱼鳞纹后粗糙度反而增大<sup>[61]</sup>,这或许与材料、加工方式、加工参数等有关,对摩擦磨损性能的影响还需更系统的研究。

Ren 等<sup>[7]</sup>、韩爽等<sup>[62]</sup>、Chen 等<sup>[63]</sup>采用超声辅助滚压、超声辅助铣削等手段处理试样,经处理后材料表层发生位错缠结、晶粒细化,粗糙度显著降低且变化更平稳,摩擦因数减小,表层显微硬度提高,表层残余压应力增大,微结构提高了材料表面滞油能力,嵌藏磨损的碎屑,降低摩擦扭矩,摩擦磨损性能显著提升。Zhu 等<sup>[64]</sup>采用超声椭圆振动织构工艺在硬质合金刀具前刀面制备出微凹槽,试验表明微凹槽刀面相比于原始刀面抗黏接性更强,切削时切屑黏附率显著降低,有效降低了摩擦面间的黏着和摩擦。巩立超等<sup>[65]</sup>对超声滚压强化机理进行了总结,轴承套圈经超声滚压处理后塑性变形产生纳米晶结构表面层,位错密度提高,晶粒细化至纳米级,表层拉应力转化为残余压应力,材料摩擦磨损性能增强。

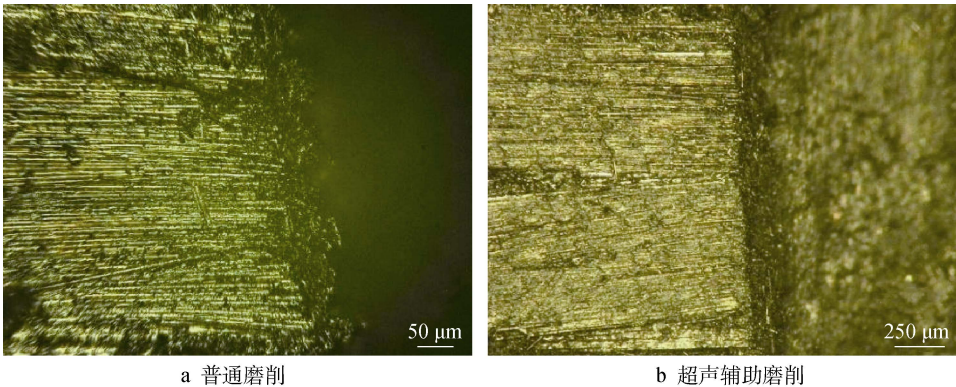


图 8 普通磨削与超声辅助磨削槽壁质量对比<sup>[53]</sup>  
Fig.8 Comparison of groove wall quality between ordinary grinding (a) and ultrasonic assisted grinding (b)<sup>[53]</sup>

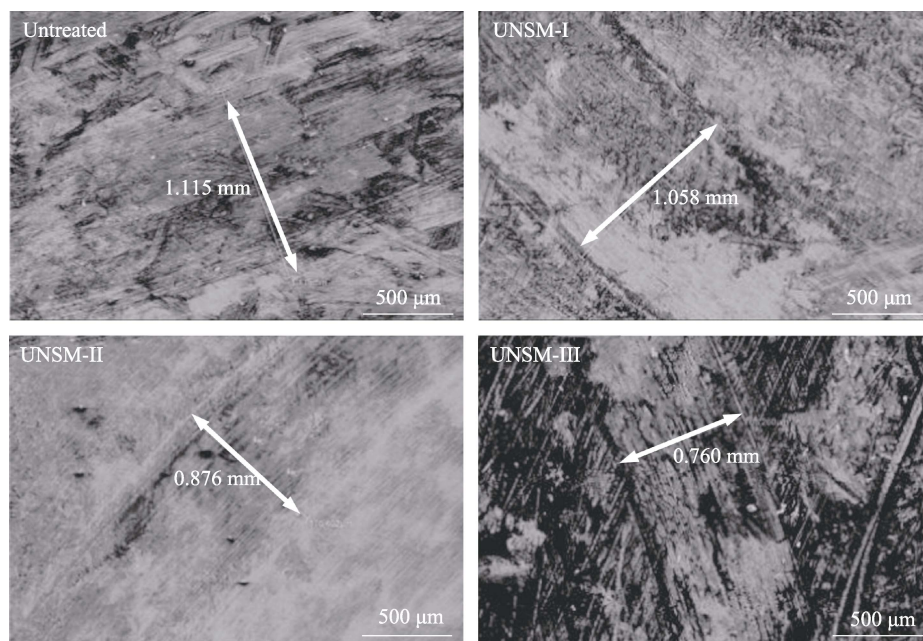


图9 AZ91D 镁合金未处理试样和超声处理试样 UNSM-I、UNSM-II、UNSM-III 滑动磨损轨迹对比<sup>[60]</sup>

Fig.9 Comparison of sliding wear tracks between untreated and ultrasonic treated UNSM-I, UNSM-II, UNSM-III AZ91D magnesium alloy samples<sup>[60]</sup>

Amanov 等<sup>[66]</sup>采用超声纳米晶表面改性技术处理轴承钢后在其表面制备出微凹坑和纳米晶结构表面层,表层晶粒尺寸随着深度的增加而增大,其表面摩擦因数减小约 25%,磨损体积减少约 60%,轴承钢的摩擦磨损性能显著提高。

### 3.2 超声辅助表面纳米化对疲劳性能的影响

疲劳性能是衡量产品使用性能的重要参考,超声振动辅助加工可诱导材料产生纳米晶结构表面层,并在表面制备出微结构,增大表层残余压应力,这些因素共同作用改善了材料疲劳性能。

Zhao 等<sup>[67]</sup>通过超声冲击轧制工艺处理 TC11 钛合金,图 10 横截面金相图显示纳米晶结构表面层金

相组织显著细化,更加致密均匀。材料表面显微硬度最高,随着深度增加硬度减小,到达芯材处趋于稳定,残余压应力在近表面取得最大值之后随着深度增加逐渐减小,最终趋于稳定<sup>[63]</sup>。

试样经超声表面滚压<sup>[68]</sup>、超声冲击<sup>[69-70]</sup>等工艺处理后塑性变形产生晶粒细化层,表层微组织细化、位错密度增大、残余压应力增大,表面显微硬度提高、粗糙度减小。如图 11 所示,超声冲击强化处理后的试样疲劳裂纹源由近表面转移至靠近中心位置疲劳裂纹萌生扩展难度增大,疲劳寿命显著增加。

### 3.3 超声辅助表面纳米化对生物学性能的影响

钛合金、钴合金、不锈钢等广泛应用于生物材料,超声振动辅助加工技术可改性生物材料的表层微组织及表观形貌,改善材料的生物学性能。

超声纳米晶表面改性技术诱导钛合金产生梯度纳米结构层,材料力学性能得到改善,钛合金表面形成微纹理,利于细胞黏附和骨结合,加强了生物与机械间的连锁<sup>[71]</sup>。Yulia 等<sup>[72]</sup>发现在碱性溶液中采用高强度超声波处理可诱导钛表面产生二氧化钛纳米泡沫,引起材料表面纳米形貌、浸润性和结晶度变化,提高了钛的亲水性、生物/细胞相容性。

Mehdi 等<sup>[9]</sup>发现超声纳米晶表面改性处理后的 Ti-29Nb-13Ta-4.6Zr (TNTZ) 合金的耐磨性比原始样本高出 7 倍以上。细胞培养试验结果如图 12 所示,MC3T3 细胞在处理过的合金表面更容易黏附、增殖,原因是晶粒细化和微观组织效应。

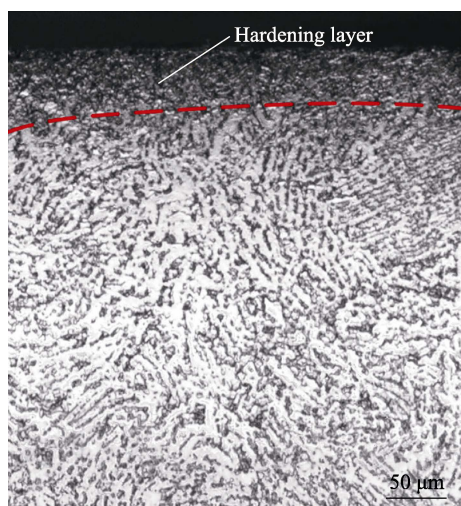


图 10 横截面金相图<sup>[67]</sup>

Fig.10 Cross-sectional metallographic diagram<sup>[67]</sup>



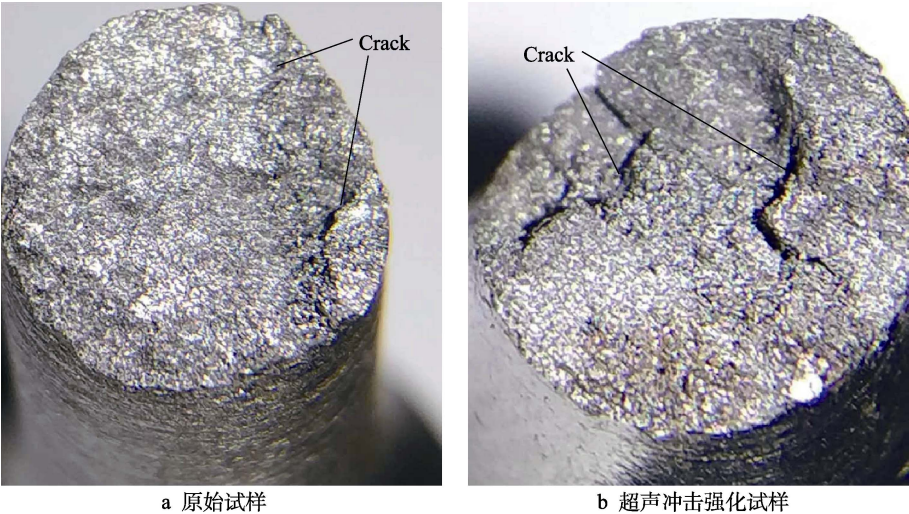


图 11 球墨铸铁试样拉伸疲劳试验对比<sup>[70]</sup>  
Fig.11 Comparison of tensile fatigue tests of nodular cast iron specimens<sup>[70]</sup>

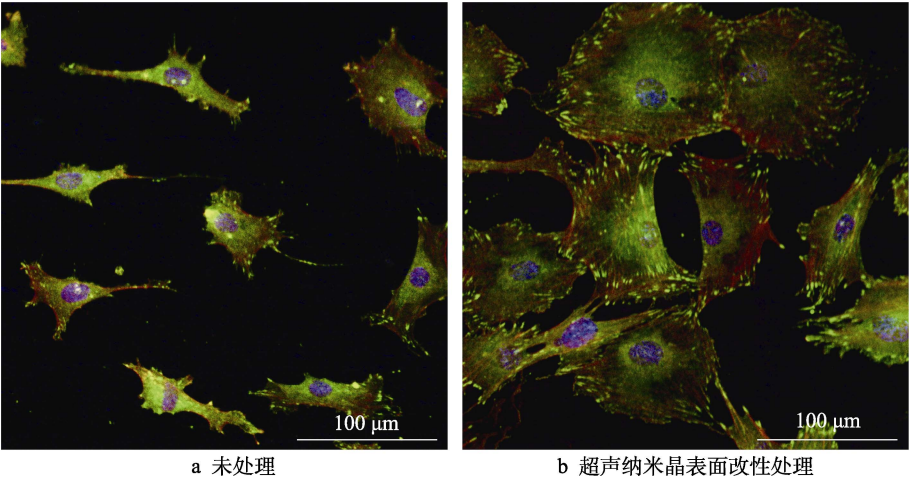


图 12 未处理与超声纳米晶表面改性处理 TNTZ 合金基底表面细胞黏附、增殖状况对比<sup>[9]</sup>  
Fig.12 Comparison of cell adhesion and proliferation on the substrate surface of TNTZ alloy between untreated (a) and ultrasonic nanocrystalline surface modification (b)<sup>[9]</sup>

3.4 超声辅助表面纳米化对表面浸润性的影响

超声振动辅助加工产生高频冲击, 刀具与工件断续接触, 可在材料表面制备出一定参数(形状、尺寸、

排布方式等)的微结构, 对表面浸润性影响显著。  
唐军等<sup>[73]</sup>分别采用铣削和纵扭复合超声铣削处理 7075 铝合金, 处理后合金表面形貌对比如图 13 所示, 超声铣削使合金表面形成鱼鳞状微结构增强了其疏水性。Sayed 等<sup>[74]</sup>发现钛合金经三维椭圆振动

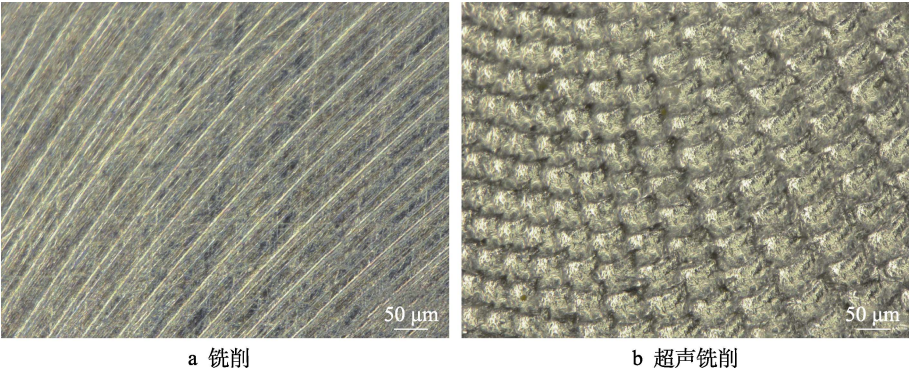


图 13 铣削与超声铣削表面形貌对比<sup>[73]</sup>  
Fig.13 Comparison of surface morphology between milling (a) and ultrasonic milling (b)<sup>[73]</sup>



车削处理后表面产生层级化纳米微结构,增加了额外的表面面积,减小了接触角,钛合金表面亲水性增强。

材料表面浸润性由微结构参数决定,并受控于超声振动模式和加工参数。Nouri 等<sup>[75]</sup>发现超声振动辅助加工工艺可在 Al7075-T6 合金表面制备出微纹理,改善和控制其表面浸润性,超声振动模式(如椭圆振动、线性振动、三维振动)和加工参数(切削速度、进给量等)决定了微纹理的形状和排列。Chen 等<sup>[76]</sup>研究了振动辅助铣削参数(振幅、频率、相位差等)对微结构形貌的影响,发现振动频率与主轴旋转频率比值为奇数时制得鱼鳞状纹理,比值为偶数时制得波纹状纹理,浸润性试验显示鱼鳞状微结构的亲水性比波纹状更强。

值得注意的是即使是同类型(如都是鱼鳞状)的微结构,在不同研究中对材料表面浸润性的影响也不尽相同,甚至截然相反,这或许与超声振动模式、振动参数、材料等有关,还需进一步深入研究。

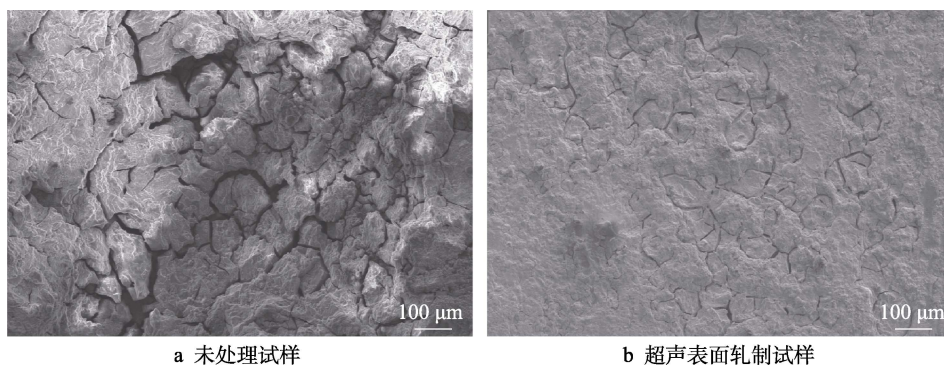


图 14 试样在 5%NaCl 水溶液中浸泡 3 d 腐蚀结果对比<sup>[78]</sup>  
Fig.14 Comparison of corrosion results of samples soaked in 5wt.%NaCl aqueous solution for three days<sup>[78]</sup>

张体明等<sup>[79]</sup>发现 2A12 铝合金经超声冲击处理后表层晶粒细化、排布更加致密,处理前后合金的腐蚀方式由点蚀和晶间腐蚀为主转为均匀腐蚀,腐蚀速率显著降低。Pandey 等<sup>[80]</sup>发现 7075 铝合金经超声喷丸处理后产生纳米晶结构表面层,表层组织更加细化、均匀,表层残余压应力增大,相比于未经超声喷丸处理的试样,腐蚀电流减小、腐蚀电位升高,材料耐腐蚀性能显著提高。

## 4 总结展望

表面纳米化诱导材料产生纳米晶结构表面层,发生晶粒细化、位错运动、相变等微观变化,显著影响材料疲劳强度、耐腐蚀性能、摩擦磨损性能、生物学性能等。分析了表面纳米化方法对晶粒、位错、金相的影响及机理,以及表面纳米化对材料性能的影响及机理,其中超声辅助表面纳米化方法因具有不需引入其他元素、不污染环境、原理简单、高速高质量、成

## 3.5 超声辅助表面纳米化对耐腐蚀性能的影响

超声振动辅助加工诱导材料产生纳米晶结构表面层,表面缺陷减少,电化学参数改善,提高了材料耐腐蚀性能。

超声辅助表面纳米化提高材料耐腐蚀性能在一定条件下具有最优值。Kumar 等<sup>[77]</sup>采用超声喷丸方法诱导 Ti-6Al-4V 合金产生纳米晶结构表面层,表面层的钝化作用提高了合金耐腐蚀性,但随着处理时间增加,耐腐蚀性提高到一定程度后开始降低,原因是过度的局部加工硬化破坏了试样表面。

Ye 等<sup>[78]</sup>发现 AZ31B 镁合金经超声表面轧制处理后发生大塑性变形产生晶粒细化层,材料表面缺陷减少减小了合金与腐蚀溶液接触面积,材料腐蚀速度降低。残余压应力提高,抵消掉部分腐蚀引起的横向拉应力,抑制了腐蚀裂纹萌生扩展。图 14 为处理前后试样腐蚀结果对比,处理后材料耐腐蚀性能显著提高。

本低廉、可依托于各种传统加工工艺等优势得到广泛应用。包括超声辅助表面纳米化在内的表面纳米化技术有待进一步发展成熟,表面纳米化与物理、化学、力学等学科的交叉融合尚不充分,对数字化仿真等技术的应用还有所欠缺,且在一定程度上仍被现有加工设备的品质、精度等因素制约,以下问题亟待解决:

1) 数字化仿真模拟技术在制造领域应用越来越广泛,但目前针对表面纳米化处理过程中纳米晶结构表面层的模拟仍极其匮乏。将模拟仿真与试验相结合,研究表面纳米化处理对微组织结构和材料性能的影响过程及机理,分析微组织结构与加工参数、微组织结构与材料性能的映射关系并建立模型直观反映,对实现纳米晶结构表面层可控、可预测进而定制材料性能使表面纳米化工艺更好地投入到生产制造中具有推动作用,这尚需更全面系统的研究。

2) 表面纳米化处理过程中常发现材料的某些性能可能不会同时达到最优值,上述映射关系可能并非单一的正相关或负相关,为了提高综合材料性能,依

托于上述模型的评价体系有待建立。

3) 纳米晶结构表面层改进材料性能的机理研究受限于现有观测手段、加工技术, 提高纳米晶结构表面层质量是持久的渐进目标。超声振动辅助加工及其他表面纳米化技术诱导产生纳米晶结构表面层的机制及基于相变动力学的高温稳定性等仍需深入分析探索。

4) 超声振动辅助加工技术的关键有超声振动单元、超声切削刀具、超声切削机床、超声系统、数控机床集成技术等, 这些因素有待不断完善, 提高超声系统的效率和功率, 新材料的开发和技术手段的改进都是重要研究内容, 对于更好地应用超声振动辅助加工技术具有深远意义。

5) 目前的表面纳米化手段普遍对材料表层影响深度较小, 制约了材料整体性能的提升。超声振动辅助加工与其他表面纳米化方法组合使用是可探讨研究之处, 优势互补或许可进一步诱导产生更优异的材料性能。

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