

纳米填料改性水泥基材料及其结构物内部界面研究进展

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摘要: 水泥基材料的黏结性能与结合界面特征决定了水泥基材料及其结构物的力学与耐久性能。纳米填料可通过界面特有的纳米富集效应在界面内部提供大量成核位点并发挥纳米中心效应, 诱导产生纳米-中心壳单元; 纳米-中心壳单元的生成有助于限制氢氧化钙晶体的定向生长并提高界面内部水化产物微观结构的致密性, 进而改善界面黏结性能。本文聚焦纳米填料对水泥基材料黏结性能与结合界面特征的改善规律和调控机制, 系统总结了界面的基本特征及纳米填料作用下界面改善的基本机制与调控规律, 分析了现存研究难点并展望了未来发展方向。纳米水泥基复合材料界面相关研究有助于揭示水泥基材料多尺度性能演化的本质机理, 也为水泥基材料及其结构物的高性能设计、数字/智能建造、维护修补与再生循环利用等方面提供理论基础与工程支撑。

关键词: 纳米填料; 水泥基材料及其结构物; 界面性能; 界面特征; 改性机制

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诺贝尔奖获得者泡利(Wolfgang Ernst Pauli)曾说过:“上帝创造了固体, 魔鬼发明了界面”, 直指界面是材料中最重要也是最复杂的问题。在边壁、单边生长、泌水等效应的作用下, 普通硅酸盐水泥基材料内部水泥石/水泥砂浆-骨料界面具有孔隙率高、晶体含量高、水化程度高等特点, 存在硬度小、强度低等固有缺陷^[1-5]。虽然传统界面的厚度仅为10~50 μm , 但由于粗细骨料的总比表面积大, 界面区可占水泥石体积分数的20%~30%^[6]。这些固有的特点与缺陷使界面成为材料中的最薄弱环节。一方面, 界面相通常是水泥基材料中最易形成裂缝的薄弱环节, 受力过程中裂纹多从界面内部萌生、扩展并连通, 进而引发宏观开裂破坏; 另一方面, 界面

结构相对疏松, 孔隙率较高, 极易成为外部水分与有害离子渗透的重要通道, 从而加速材料劣化, 削弱其耐久性^[7-10]。与水泥基材料内部水泥石/水泥砂浆-骨料界面类似, 新-旧水泥基材料界面、增强筋-水泥基材料界面等黏结界面也是结构中的薄弱区域, 在很大程度上决定了结构性能^[11-13]。例如, 新-旧水泥基材料界面黏结能力不足, 使修补材料难以与基体形成有效锚固, 裂缝易沿界面萌生并扩展, 导致修补层开裂、剥离甚至整体失效, 从而大幅降低结构的使用寿命和维修效果^[14]。钢筋或纤维增强塑料(FRP)筋与水泥基材料之间界面的良好黏结是两者共同工作的基础。当界面滑移或脱黏发生时, 应力无法由水泥基材料有效传递至增强筋, 从而显著

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降低结构的承载力和延性，最终导致结构失稳或脆性破坏^[15]。此外，钢筋–水泥基材料界面作为钢筋锈蚀直接发生的微环境，其微观结构直接决定了钢筋的锈蚀行为^[16–17]。理想情况下，钢筋–混凝土界面可以为钢筋提供物理与化学保护使其免受腐蚀介质侵蚀。理想的钢筋–混凝土界面可以有效阻断腐蚀介质与钢筋表面接触，同时在钢筋表面会产生一层 5~15 nm 的钝化保护膜，保护钢筋免受腐蚀介质侵蚀^[18–19]。因此，界面退化与失效是导致水泥基材料

力学和耐久性能退化、修补失效、结构承载力劣化的主要原因之一(表 1)。然而，界面性能受黏贴相特征、表面粗糙度、配合比、养护方式、服役条件等多变量同时影响，且同一种增强方式在不同界面中表现也不同，不同增强策略之间可能存在协同或干扰，调控设计需综合优化^[20]。基于界面问题的复杂性与重要性，优化水泥基材料黏结性能与结合界面特征，是调控结构与性能的难点，也是增强水泥基材料及其结构物力学和耐久性能的核心策略之一。

表 1 界面黏结性能不足导致的典型工程问题

Table 1 Typical engineering issues caused by inadequate interfacial bond properties

Engineering scenarios	Interface types	Interfacial failure modes and their impacts
Mechanical property degradation of conventional cement-based materials ^[21–22]	Cement paste-aggregate interface	Crack initiation and propagation zones where aggregates cannot be effectively bonded into an integral structure
	Cement paste-fiber interface	Insufficient interfacial bond leading to fiber slip and pulling-out, resulting in failure of the bridging effect
Durability deterioration of conventional cement-based materials ^[23]	Cement paste-aggregate interface	Loose and porous interfacial characteristics providing pathways for aggressive agents (<i>e.g.</i> , chloride ions, sulfate, and carbon dioxide)
	Steel reinforcement-cement-based material interface	Reinforcement corrosion-induced expansion causing bond failure between steel reinforcement and cement-based materials, leading to loss of reinforcement effectiveness
Insufficient performance of recycled concrete ^[24]	Old cement paste-aggregate interface	Multiple interfacial regions prone to crack initiation and propagation, resulting in reduced strength and durability
	New-to-old cement-based material interface	
Insufficient performance of 3D-printed concrete ^[25]	Interlayer interface	Cold joints, weak bond, and interlayer delamination adversely affecting the mechanical performance and durability of the material and structure
Failure of prefabricated structural joints ^[26]	New-to-old cement-based material interface	Poor bond and interfacial slip leading to interlayer displacement and joint cracking, reducing structural ductility and integrity
Leakage and deterioration of bridge expansion joints ^[27]	New-to-old cement-based material interface	Interfacial bond failure and cracking under fatigue loading and temperature effects, resulting in leakage, corrosion, and freeze-thaw damage
Interlayer debonding in pavement structures ^[28]	Base-surface interface in pavement structures	Interlayer shear failure under traffic loading due to insufficient bond, reducing overall load-bearing capacity
Failure of supporting structures ^[29]	Shotcrete-rock interface	Shear slippage caused by inadequate bond performance, compromising the stability of tunnel or slope support systems
Failure of structural strengthening systems ^[30–31]	New-to-old cement-based material interface	Formation of new cracks due to insufficient interfacial bond strength
	Cement-based material-FRP/steel plate interface	Interfacial debond preventing the reinforcing phase from functioning effectively, resulting in strengthening failure

水泥基材料及其结构呈现出显著的多尺度结构特征。从宏观角度来看，其可近似视为一种连续均质介质；在细观尺度上，材料则由水泥石基体、粗细骨料、增强筋等增强组分以及各类界面相共同构成，呈现出非均质的复合材料/结构特征；在微观尺度上，水泥石内部包含未水化水泥颗粒、水化产物[如水化硅酸钙(C-S-H)凝胶与氢氧化钙(CH)晶体]等。进一步而言，C-S-H 凝胶是由大量 C-S-H 基本粒子堆积所构成的纳米级非晶结构体系，呈现出复杂的孔隙结构和力学响应特性^[32–33]。通常，特定尺度的结构与性能受其次一级尺度结构与性能的显著

影响，如果从最根本尺度——纳米尺度，来调控水泥基材料的微观结构，有助于改善水泥基材料界面黏结性能，显著增强水泥基材料及其结构物的整体性能表现^[34–35]。这种“自下而上”的调控理念在改善界面这一细观结构时，可避免传统“自上而下”方法中因多种类界面响应不同步所引发的协调性问题，因而具有更强的普适性。

随着纳米科学的不断进步，基于纳米技术的界面改性策略逐渐应用于水泥基材料中，展现出良好的应用前景^[36–39]。纳米填料可通过界面特有的纳米富集效应在界面内部提供大量成核位点并发挥纳米

中心效应,促进大量纳米-中心壳单元的形成。这一过程有助于诱导 C-S-H 在界面区域有序聚集,提升界面结构的致密性,同时有效抑制 CH 晶体的生长,改善界面黏结性能^[40-42]。因此,本文系统回顾了传统界面的基本特征、纳米填料对界面的改性机理以及纳米填料对界面的改性效果;基于对现有研究进展的客观评估,理清现存关键科学问题与技术瓶颈并提出未来发展方向。

1 纳米填料对界面的影响效果

1.1 纳米填料对界面黏结性能的影响效果

纳米填料的引入能够有效增强水泥石-骨料和水泥砂浆-骨料界面的黏结性能,其提升幅度在 60% 以上^[42-44]。如图 1^[42]所示,复合填料可使水泥石-骨料界面的黏结强度提高 50.0%~65.3%。复合 2%

纳米二氧化硅可使水泥石-骨料的剪切黏结强度提升 165.1%^[45]。此外,研究表明,当掺入 2% 纳米氧化锆、0.3% 镀镍多壁碳纳米管和 0.3% 纳米氮化硼后,水泥砂浆-骨料界面黏结强度分别提高 35.1%、38.8% 和 42.8%^[43]。另一项研究系统评估了纳米氧化铝、纳米高岭土和纳米二氧化硅对界面抗拉黏结性能的影响。结果表明,3% 纳米氧化硅和 3% 纳米高岭土可使界面抗拉黏结强度分别提升 108.5% 和 43.4%。相比之下,纳米氧化铝对界面抗拉黏结性能的提升效果仅为 20%^[46]。同时,纳米填料增强水泥石-骨料和水泥砂浆-骨料界面黏结性能的能力与其几何维度密切相关,整体表现为:二维纳米填料>一维纳米填料>零维纳米填料。

纳米填料的引入还可有效改善新-旧水泥基材料界面。如图 2 所示,复合纳米填料后,新-旧水泥

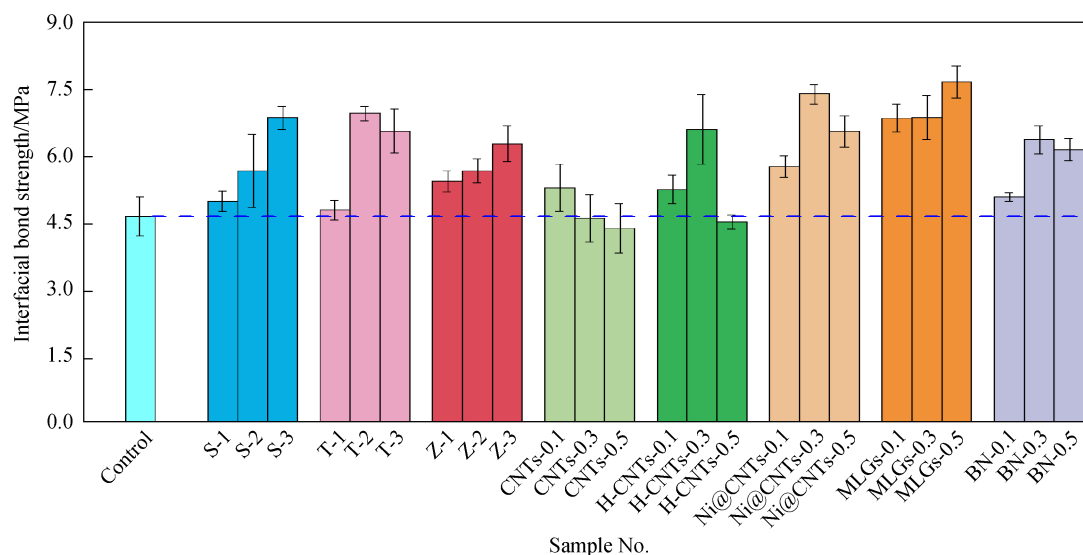


图 1 纳米填料改性水泥石-骨料界面黏结强度^[42]

Fig. 1 Interface bond strength of cement paste-aggregate interface modified with nanofillers^[42]

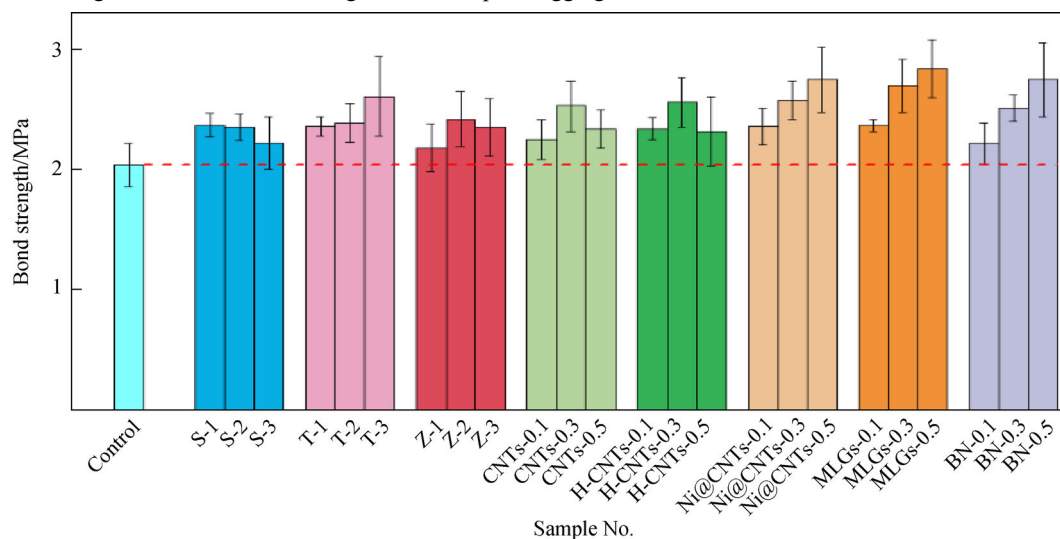


图 2 纳米填料改性新-旧水泥基材料界面黏结强度^[36]

Fig. 2 Interface bond strength of new-to-old cement-based materials modified with nanofillers^[36]

基材料的界面黏结强度提升了 27.8%~39.0%^[36]。与水泥石-骨料和水泥砂浆骨料界面类似, 纳米填料的增强效果主要与其几何结构维度相关, 具体表现为: 二维纳米填料>一维纳米填料>零维纳米填料。Deng 等^[47]通过纳米压痕技术表征了不同纳米纤维素剂量下新旧骨料-基体界面的弹性模量分布。结果表明, 旧界面的力学性能优于新界面, 在新界面处观察到显著的低弹性模量区域。由于水泥颗粒在水泥石-再生骨料界面处的水化程度增加, 掺入适量的纳米纤维素可以显著改善新界面的纳米力学性能。

纳米填料在调控水泥基材料与增强筋之间的黏结-滑移行为方面也展现出显著效果, 不仅有助于增强界面黏结强度, 还能明显抑制滑移现象^[37, 48–49]。如图 3 所示^[37], 相较于未掺纳米填料的对照组, 加入纳米填料后, 水泥基材料与钢筋之间的开裂黏结强度提高了 20.5%, 极限黏结强度增加了 10.3%, 残余黏结强度则上升了 22.4%; 且极限滑移和残余滑移分别减少了 56.5%和 52.1%。上述结果说明, 纳米填料通过改善界面微结构及增强微观力学相互作用, 可有效提升钢筋与水泥基体之间的协同变形能力与黏结性能, 从而有助于提高整体复合体系的力学稳定性。类似地, 纳米填料的引入显著改善了水泥基材料与 FRP 筋间的黏结性能与滑移行为^[21]。对于水泥基材料-玻璃纤维增强复合材料(GFRP)筋界面, 纳米填料的掺入使极限黏结强度提升 3.11 MPa(16.4%), 残余黏结强度提高 3.47 MPa(27.8%); 极限黏结滑移和残余黏结滑移分别减少 0.365 mm(28.7%)和 0.758 mm(23.3%)。对于碳纤维增强复合材料(CFRP)筋, 纳米填料带来的增强效果更为显著: 极限黏结强度提高 12.37 MPa(37.8%),

残余黏结强度提高 9.47 MPa(42.9%); 同时, 极限滑移和残余滑移分别减少 2.274 mm(40.0%)和 3.182 mm(32.9%)。上述研究证实了纳米填料在提升水泥基材料结构承载能力方面的显著潜力。

1.2 纳米填料对界面特征的影响效果

纳米填料对水泥石-骨料和水泥砂浆-骨料界面特征的影响主要包括 4 个方面: 物相性质、界面厚度、晶体尺寸和密实程度。如图 4 所示, 复合纳米填料可使界面内部物相的平均压痕模量由水泥石内部物相的 70%提升至 83%~98%, 平均硬度也由水泥石的 59%提高至 68%~141%。进一步通过对压痕区域的观察发现, 复合纳米填料不会明显改变该处物相的模量, 但其硬度却出现了显著提高, 这表明可能生成了新型水化产物——纳米中心效应诱导产生的超硬 C-S-H 凝胶相^[50]。Gao 等^[51]通过原子力显微镜(AFM)对界面物相的微观力学性能进行了分析, 发现掺加纤维素纳米纤维后, 界面内部物相的平均弹性模量提升了约 36.7%。Zhang 等^[52]系统研究了纳米氧化硅掺量对水泥石及界面弹性模量的影响。结果显示, 在掺入 1%(质量分数)纳米氧化硅的条件下, 水泥石和界面的弹性模量分别较空白组提高了 73.5%和 90.5%。值得注意的是, 随着纳米填料掺量的进一步增加, 其增强效果并未持续提升, 反而出现一定程度的力学性能下降, 主要归因于纳米颗粒在体系中的团聚现象, 进而削弱其有效分散和界面增强作用^[53]。纳米填料的掺入可显著减小界面厚度, 抑制金属阳离子在界面处的富集, 提高界面内部 C-S-H 凝胶的钙硅比^[42]。复合纳米填料后, 水泥石-骨料界面厚度可由 18 μm 减少至 9~12 μm , 界面内 C-S-H 凝胶的钙硅比则提高至 0.75~1.12, 如图 5 所示^[43]。需要指出的是, 纳米填料对水泥石基体的钙硅比影响不大。Liu 等^[54]和 Xiao 等^[55]通过能量散射光谱(EDS)测量 Ca/Si 摩尔比随骨料间距的变化, 发现纳米二氧化硅可以有效地减小界面厚度。当水灰比为 0.3 时, 复合纳米二氧化硅使界面的厚度从 50 μm 减小到 20 μm 。此外, 还有研究利用 SEM 观察了试件破坏后界面的微观结构(见图 5)^[56]。结果表明, 在未添加纳米填料的样本中, 界面区域存在大量片状 CH 晶体, 其粒径可达约 55 μm 。而在掺入复合纳米填料后, 水泥石-骨料界面微观结构显著致密化, CH 晶体数量减少且尺寸分别缩小至 9~32 μm 。Palla 等^[57]和 Durgun 等^[58]通过 SEM 证明, 掺入纳米二氧化硅后提高了界面的致密性, 且不存在大量 CH 晶体。

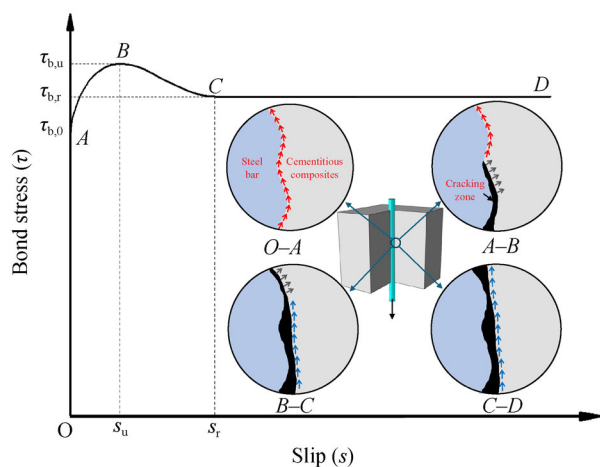


图 3 钢筋-水泥基材料界面黏结-滑移曲线^[37]

Fig. 3 Bond slip curve of steel bar-cement-based material interface^[37]

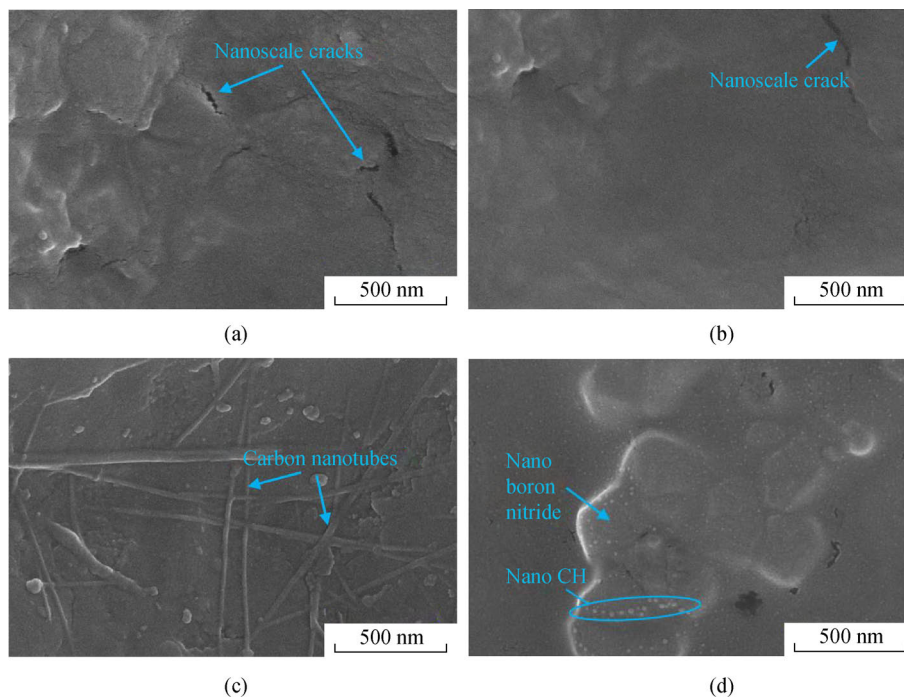


图 4 界面物相压痕痕迹微观形貌。(a) 空白组, (b)复合 3%(质量分数)纳米氧化硅, (c) 复合 0.3%镀镍多壁碳纳米管, (d) 复合 0.3%纳米氮化硼^[50]

Fig. 4 Microscopic morphology of indentation marks on interface. Microstructure of (a) blank group, (b) adding 3% (mass fraction) nano silica, (c) adding 0.3% nickel plated multi walled carbon nanotubes, (d) adding 0.3% nano boron nitride^[50]

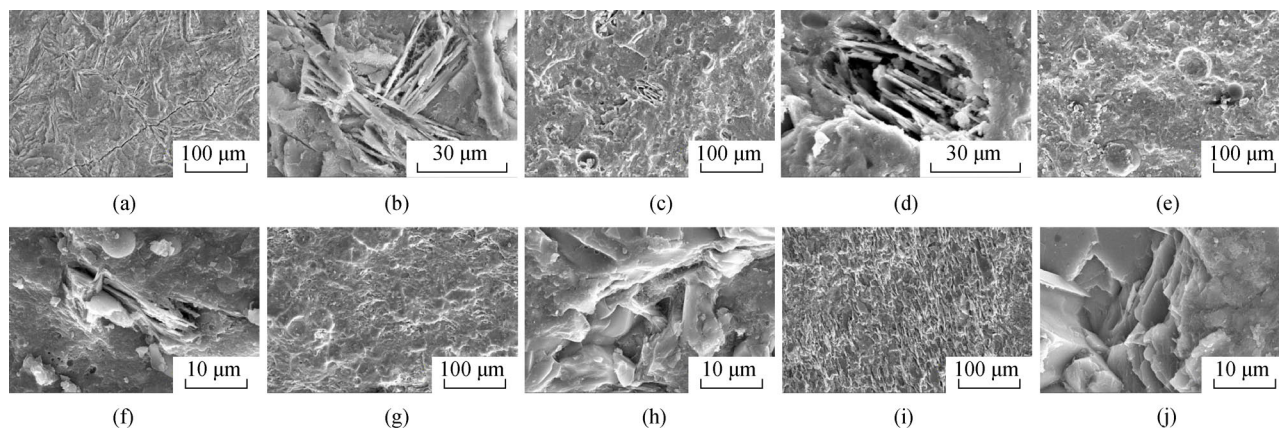


图 5 水泥石侧界面微观形貌。(a)和(b) 空白组界面微观形貌(1000×)和(5000×), (c)和(d) 掺入 3%纳米氧化硅后界面微观形貌(1000×)和(5000×), (e)和(f) 掺入 2%纳米氧化钛后界面微观形貌(1000×)和(5000×), (g)和(h) 掺入 0.3%镀镍多壁碳纳米管后界面微观形貌(1000×)和(5000×), (i)和(j) 掺入 0.5%多层石墨烯后界面微观形貌(1000×)和 (5000×)^[43]

Fig. 5 Microscopic morphology of the cement stone side failure surface of interface. Microscopic morphology of (a) and (b) control group (1000×) and (5000×), (c) and (d) interface with 3% nano silica (1000×) and (5000×), (e) and (f) interface with 2% nano titanium oxide (1000×) and (5000×), (g) and (h) interface with 0.3% nickel plated multi walled carbon nanotubes (1000×) and (5000×), (i) and (j) interface with 0.5% multilayer graphene (1000×) and (5000×)^[43]

纳米填料对新-旧水泥基材料界面也有显著影响。如图 6 和图 7 所示^[34], 在对照组中, 新-旧水泥基材料界面区域可见大量片状或柱状 CH 晶体析出, 界面微观结构疏松; 且在旧水泥基材料表面中观察到大量毛细孔。相比之下, 纳米填料的引入显著改善了界面区的微观结构特性。具体表现为: 界面水化产物趋于致密, CH 晶体含量大幅减少, 原先位于旧水泥基体表面的毛细孔隙被新水泥材料中

的水化产物有效填充, 界面结构连续性显著增强。添加纳米氧化硅可使新-旧水泥基材料界面孔隙率由 24%降低至 16%^[59]。同时, 通过元素分布分析还观察到纳米颗粒在新-旧水泥基材料界面内存在明显的局部富集现象, 特别是钙硅比显著提升^[60]。Zhang 等^[61]采用纳米氧化硅对再生骨料进行预处理, 研究其对新-旧水泥基材料界面厚度的影响。结果显示, 该方法可使新生成的界面厚度减少约 10%~20%。

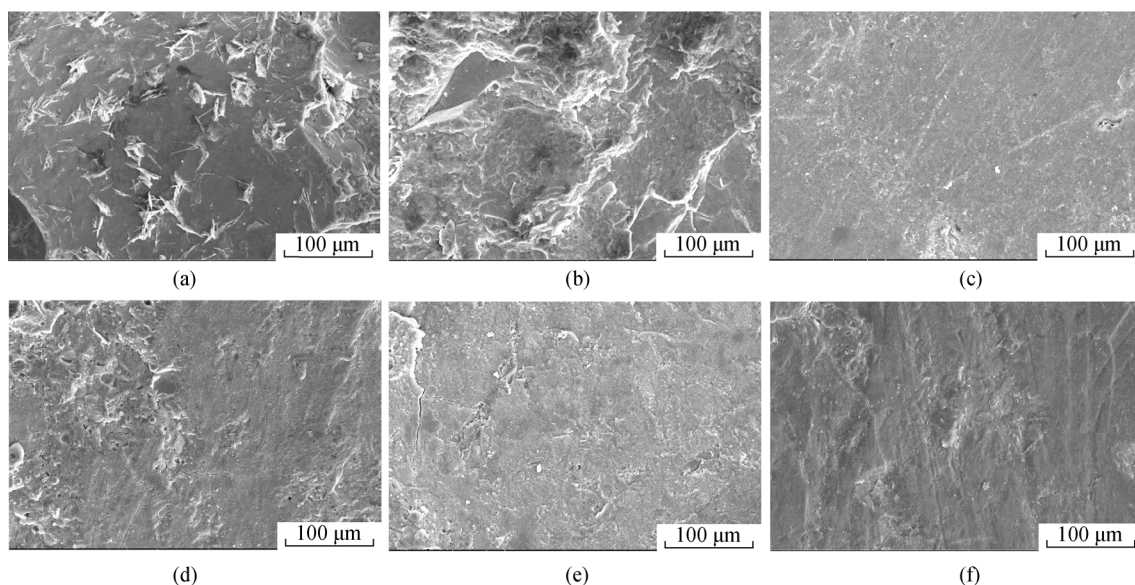


图6 新-旧水泥基材料界面新水泥基材料侧断裂面微观形貌(1000×)。(a) 空白组, (b) 复合 1%纳米氧化硅, (c) 复合 3%纳米氧化钛, (d) 复合 0.5%镀镍多壁碳纳米管, (e) 复合 0.5%多层石墨烯, (f) 复合 0.5%纳米氮化硼^[34]

Fig. 6 Micro-morphology of the fracture surface on the side of new cement-based materials at the interface of new-old cement-based materials (1000×). (a) Blank group, and the addition of (b) 1% nano silica, (c) 3% nano titanium oxide, (d) 0.5% nickel plated multi walled carbon nanotubes, (e) 0.5% multilayer graphene, (f) 0.5% nano boron nitride^[34]

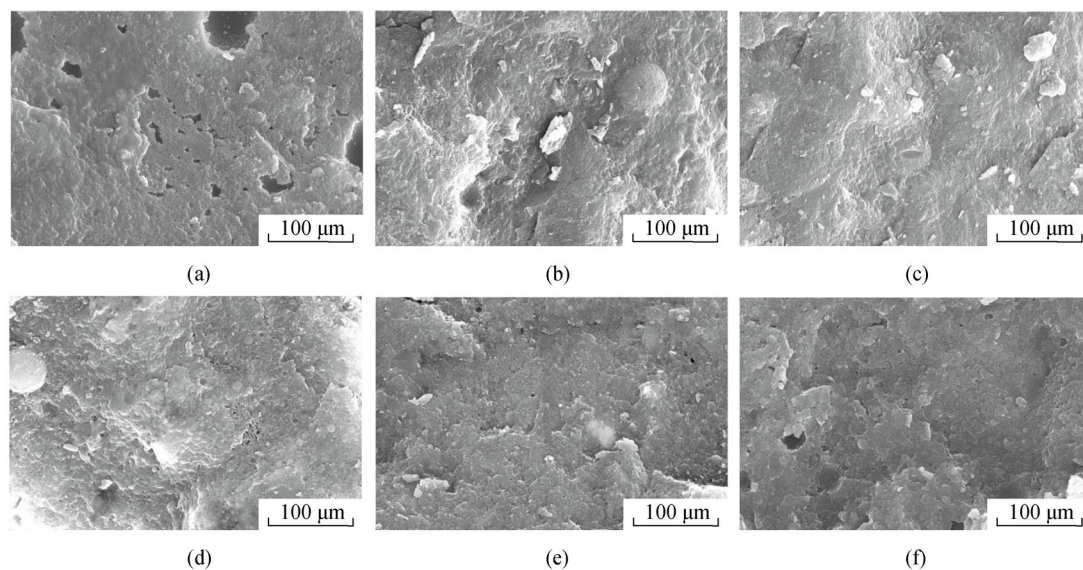


图7 新-旧水泥基材料界面旧水泥基材料侧断裂面微观形貌。(a) 空白组, (b) 复合 1%纳米氧化硅, (c) 复合 3%纳米氧化钛, (d) 复合 0.5%镀镍多壁碳纳米管, (e) 复合 0.5%多层石墨烯, (f) 复合 0.5%纳米氮化硼^[34]

Fig. 7 Fracture surface on the old cement-based materials side at the interface between the old and new cement-based materials. (a) Blank group, (b) addition of 1% nano silicon oxide, (c) addition of 3% nano titanium oxide, (d) addition of 0.5% nickel plated multi walled carbon nanotubes, (e) addition of 0.5% multilayer graphene, (f) addition of 0.5% nano boron nitride^[34]

纳米填料可优化水泥基材料与增强筋界面的微观结构和元素组成。如图8所示^[20, 35], 纳米填料的引入可显著提升增强筋下侧界面内 C-S-H 凝胶的钙硅比, 从而改善该区域的水化产物结构。当复合纳米填料后, 钢筋下侧界面处 C-S-H 凝胶的钙硅比由原始的 0.73 提升至 0.89~1.02, 表明纳米填料能有效调控界面水化产物的组成与结构致密性。

2 界面的纳米改性机制

纳米填料对界面的改性机制包括: 富集效应与纳米中心效应^[5]。

2.1 富集效应

图9展示了纳米填料在界面中形成富集层的机理^[43]。首先, 在边壁效应的驱动下^[62], 新拌水泥石

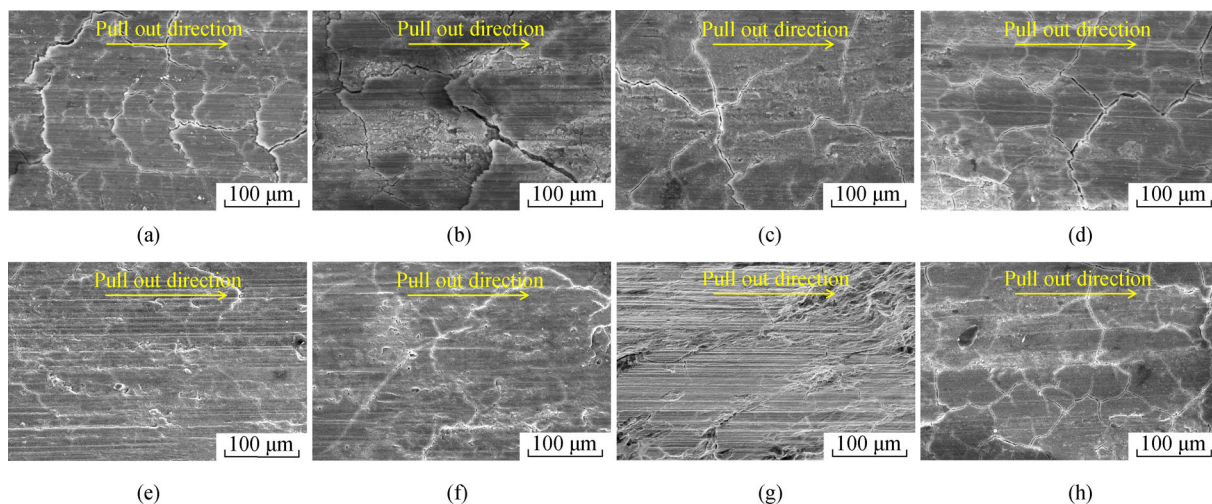


图 8 水泥基材料—增强筋界面微观形貌(1000×)。(a)和(b) 空白组上侧和下侧界面微观形貌, (c)和(d) 掺入 3%纳米氧化钛后上侧和下侧界面微观形貌, (e)和(f) 掺入 0.5%羟基化多壁碳纳米管后上侧和下侧界面微观形貌, (g) 掺入 0.5%纳米氮化硼后上侧界面微观形貌, (h) 掺入 0.5%纳米氮化硼后下侧界面微观形貌^[20, 35]

Fig. 8 Microscopic morphology of cement-based material-steel bar interface (1000×). Microscopic morphology of (a) upper interface and (b) lower interface in control group, (c) upper interface and (d) lower interface after adding 3% nano titanium oxide, (e) upper interface and (f) lower interface after adding 0.5% hydroxylated multi walled carbon nanotubes, (g) upper interface and (h) lower interface after adding 0.5% nano boron nitride^[20, 35]

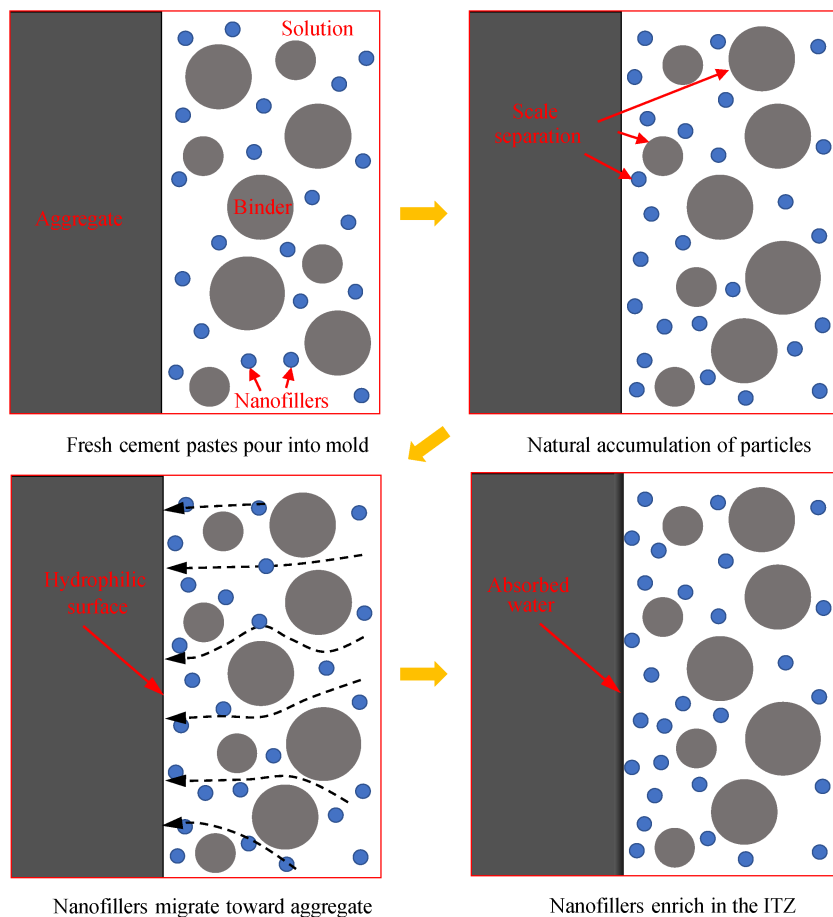


图 9 纳米填料的界面富集效应^[43]

Fig. 9 Nanofiller enrichment effect at interface^[43]

中的细小颗粒倾向于向骨料/增强筋表面迁移, 而相对较大的颗粒则趋向于远离骨料表面。这一粒径相

关的分布行为导致骨料—水泥石/钢筋界面处出现明显的尺度分离现象。在此基础上, 具有吸水性的黏

贴相表面的毛细孔吸收浆体中的水分,形成毛细抽吸效应,促使纳米尺度的填料在液相中沿胶凝颗粒之间的孔隙迁移,即纳米迁移效应。在边壁效应引起的尺度分离与水分驱动的纳米粒子迁移共同作用下,纳米填料最终在界面区域实现显著富集。这种富集增加了纳米填料在界面中的分布密度,为纳米填料改善界面微观结构和黏结性能提供了物质基础。

2.2 纳米中心效应

纳米中心效应包括纳米效应和中心效应^[63]。纳米效应指纳米填料自身所具有的超小粒径与高比表面积。超小粒径使得纳米填料在低掺量复合条件下,也能在水泥基材料内部广泛大量分布。高比表面积使得纳米填料处于高表面能状态,具有强物理化学反应活性,有助于其介入和调控水化反应和晶体生长过程。超小粒径和高比表面积是纳米填料调控水泥基材料的基础^[64]。

在纳米效应的基础上,纳米填料可在水泥基材

料内部发挥中心效应,主要包括:吸附效应、填充效应、火山灰效应、导热效应、自养护作用、钉扎效应与桥连效应、短程效应。

1) 吸附效应

根据单边生长理论,在早期水化过程中, Ca^{2+} 和 Mg^{2+} 会向骨料表面扩散^[56],富集于界面的纳米填料能够吸附包括 Ca^{2+} 和 Mg^{2+} 在内的多种阳离子。由于配位数的限制,钙离子难以在界面处形成类似方解石结构的氢氧化钙晶体,同时不阻碍其促进C-S-H的吸附和成核,最终形成大量纳米中心-壳结构单元(图10)^[42]。由于吸附阳离子的机理存在差异,不同种类的纳米填料对阳离子的吸附机制存在差异。对于纳米氧化物(如纳米氧化硅、纳米氧化钛、纳米氧化锆),其表面的活性氧能与硅氧四面体发生化学键合;而碳基纳米材料(如碳纳米管、石墨烯),则主要通过物理吸附的方式吸附阳离子^[50]。这些差异性吸附机制对填料与水化产物间的界面作用与结构演化具有重要影响。

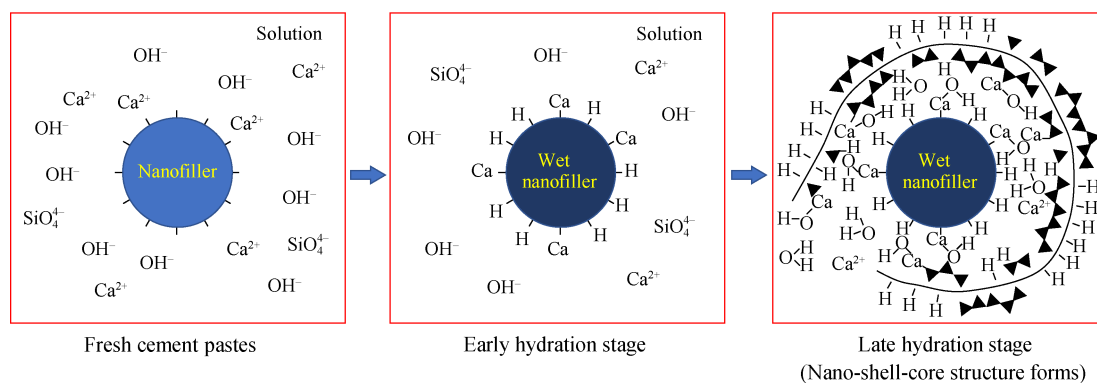


图10 纳米中心-壳单元^[42]
Fig. 10 Nano-core-shell element ^[42]

2) 填充效应

纳米填料能够填补界面中胶凝材料颗粒之间的孔隙,从而提升该区域的堆积密实度,进而降低硬化后界面的孔隙率^[65]。这种填充作用主要依赖于纳米尺度的中心-壳结构单元对界面内部微孔隙的间接填充,而并非由纳米颗粒本身直接填满这些孔隙。尽管纳米填料的颗粒尺寸极小,且掺量通常较低,其所产生的微观结构优化效应依然能在一定程度上改善界面黏结性能^[5]。

3) 火山灰效应

纳米氧化硅等具有火山灰活性的纳米填料可与CH晶体发生反应,生成C-S-H凝胶。这一反应过程有助于减少界面内CH晶体的数量、尺寸及其定向生长,从而有效优化界面的微观结构^[66]。

4) 导热效应

碳纳米管、石墨烯等具有高导热性的一维与二维纳米填料能够在水化初期有效传导水化反应释放的热量,从而使水泥石-骨料/增强筋界面的温度场分布更加均匀。这种热传导作用有助于缓解界面内部因温差引起的热应力,显著降低初始裂缝的产生风险^[67]。

5) 自养护/内养护作用

具有一定吸水能力的纳米填料(如纳米纤维素)富集到界面时,能够在水化初期吸收自由水,从而降低界面区域的实际水胶比^[66]。随着水泥水化反应消耗自由水,纳米填料与水泥基材料基体界面间形成显著的湿度梯度,纳米材料可缓慢释放先前吸收的水分,从而起到一定的内养护作用,有助于缓解

早期干缩并优化界面微结构(图 11)^[5]。

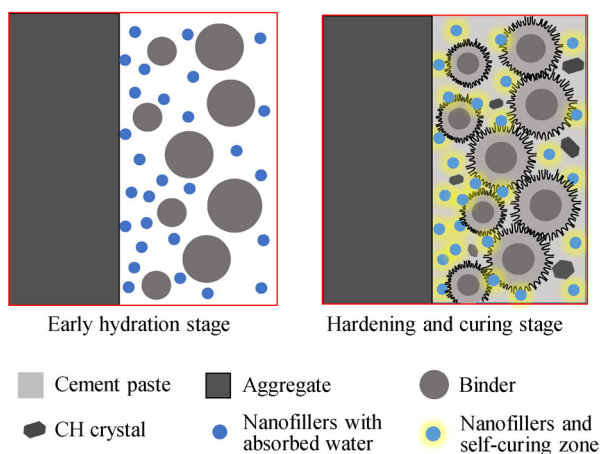


图 11 界面处纳米填料的自养护作用^[5]

Fig. 11 Self-curing effect of nanofillers at interface^[5]

6) 钉扎效应与桥连效应

在外荷载作用下, 复合纳米填料的界面表现出明显的钉扎效应^[67]。零维纳米填料形成的纳米中心-壳结构单元有助于延缓微裂纹的起始并限制其扩展路径, 从而增强界面区的黏结性能^[20, 35]。此外, 一维或二维纳米填料在界面区还表现出桥连效应。在承受外力时, 纳米填料可在小范围内桥连裂缝, 直至其被拔出或拉断, 从而提升界面黏结强度^[34]。

7) 短长程效应

研究表明, 纳米填料在水泥基材料中具有短程和长程效应, 如图 12 所示^[5, 40, 50, 68]。一方面, 纳米填料与吸附的水化产物结合, 形成纳米中心-壳结构单元。由于内部坚硬纳米中心的存在, 纳

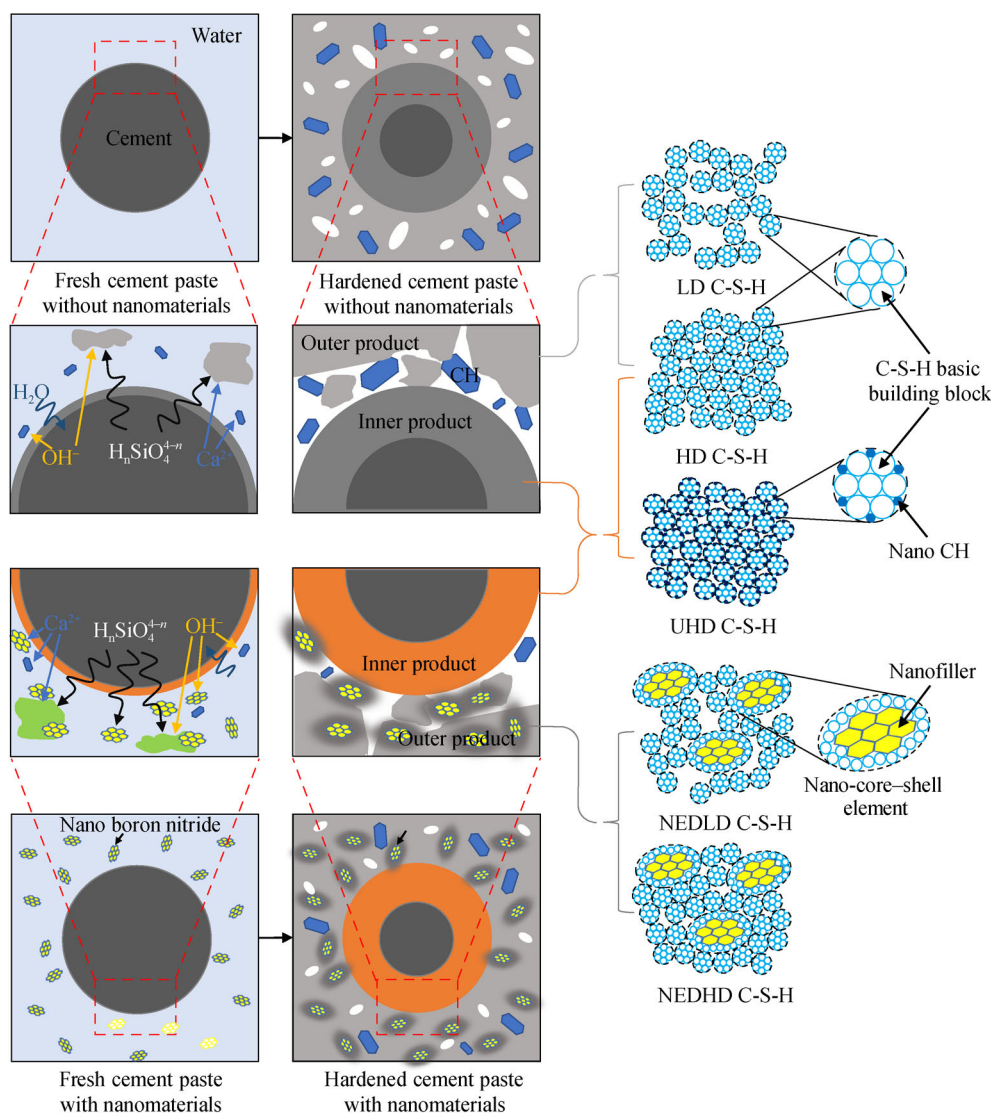


图 12 纳米填料在界面处的短长程影响机制^[50]

Fig. 12 Short and long-range effect of nanofillers in interface^[50]

米中心–壳结构单元在短程内可改变水化产物的纳米结构与性能。另一方面，纳米填料可以吸附水泥早期水化溶液中的离子，从而细化和优化纳米填料颗粒附近的水化产物。此外，纳米中心–壳结构单元和周围的 C-S-H 基本单元通过粒子间

的相互作用增强了 C-S-H 凝胶的完整性，从而提高了 C-S-H 凝胶在低堆积密度下的纳米级力学性能^[50]。

基于上述对界面的纳米改性机制总结，表 2 列出了代表性纳米材料对界面的改性机制及效果。

表 2 代表性纳米填料对界面的改性机制及效果

Table 2 Modification mechanisms and effects of representative nanofillers on interfaces

Type	General modification mechanisms and effects	Specific modification mechanisms and effects
Reactive nano-oxides (e.g., nano-silica)	Enrichment effect: increases the amount of nanofillers in the interfacial zone, providing a basis for improving the interfacial microstructure and bond properties	Pozzolanic effect: reacts with CH to generate C-S-H, reducing the size and quantity of CH crystals and optimizing the interfacial structure
Inert nano-oxides (e.g., nano-titania, nano-zirconia)	Adsorption effect: promotes C-S-H adsorption and nucleation, forming nano-core-shell elements Filling effect: enhances interfacial compactness and reduces porosity	Pinning effect: delays the initiation and propagation of microcracks, enhancing interfacial bond performance
Carbon-based nanomaterials (e.g., carbon nanotubes, graphene)	Short-range and long-range effect: Nanofillers can modify the nanostructure and properties of hydration products in a short range, and refine and optimize the hydration products near nanofillers in a long range	Thermal conductivity effect: homogenizes the temperature distribution in interfacial zone, alleviating thermal stress and reducing early-age cracking
Nano boron nitride		Bridging effect: bridges microcracks and improves interfacial bond strength
Nanocellulose		Self-curing effect: absorbs water in the molding stage and release water in the curing stage, mitigating early-age shrinkage and optimizing interfacial microstructure

3 挑战与发展方向

界面作为水泥基材料及其结构物性能控制的关键部位，在很大程度上决定了材料与结构的整体性能，但界面相关研究存在以下挑战：1) 其物理结构与力学行为高度依赖于微观尺度下的材料微观结构与多场耦合效应。然而，现有研究中关于纳米尺度界面的结构、组成、力学响应与演化机制的系统表征方法仍较为匮乏。当前对界面的观察多依赖于 SEM、EDS、X 射线衍射(XRD)及纳米压痕等技术手段，但这些方法在空间分辨率、元素灵敏度、三维重构能力以及动态演化过程解析等方面存在较大限制。例如，纳米填料在界面区的空间分布、富集行为、协同作用模式及对水化产物形成的动态调控过程仍难以直接捕捉。更为关键的是，多数手段仅能获取静态截面信息，无法实现对界面演化过程的实时追踪与多尺度、多物理场下的综合解析，严重制约了对其形成机制的深入理解。2) 由于界面具有典型的几何不连续性、结构不均匀性及化学梯度特征，其本征异质性极大增加了量化建模的难度，现有模型往往仅能描述平均性能，难以捕捉界面局部极端薄弱点或纳米尺度作用力传递路径。理论的缺失进一步导致界面性能定量模型化面临困难。尽管现有研究已明确了纳米填料可增强界面黏结性能的

现象，但尚无法建立基于材料类型、掺量、水灰比等参数建立定量预测模型，难以对界面黏结强度、滑移行为、局部裂纹扩展路径等性能实现精准调控。3) 随着多功能纳米填料(如具有高导电、高导热、自修复特性)的引入，界面的多物理场耦合行为日益复杂，如何在力、热、电、化学等多场之间建立统一耦合模型，仍是一项巨大的挑战。4) 将纳米填料改性水泥基材料及其结构物界面研究成果工程化应用仍面临困境。一方面，多数研究集中于理想试件尺度或小型构件测试，缺乏系统的工程尺度界面性能评价体系；另一方面，纳米填料本身在大规模生产与均匀分散方面仍存在一定技术困难，其在复杂工况(如潮湿、盐蚀、冻融、疲劳)下的界面稳定性也鲜有系统性研究。

针对当前纳米填料改性水泥基材料及其结构物界面研究中存在的表征困难、改性机制不明、定量模型缺失与工程应用前景等问题，未来的发展应聚焦于多手段融合的新型表征技术体系构建、机制性认知深化、智能化建模与设计，以及面向实际应用场景的功能集成与工程转化路径探索，主要包括：1) 有必要发展具备高时空分辨率的新型界面表征手段，实现对界面结构演化的全周期追踪。例如，可引入同步辐射 X 射线断层扫描成像(SRCT)、X 射线计算机断层成像(XCT)等先进表征技术，辅以时

间序列信息采集,实现界面结构、组分、晶体转变与裂纹演化过程的动态解析。2) 结合 AI 驱动的图像识别与定量分析算法,可实现高通量数据提取与异质界面特征识别,推动从定性观察向量化分析的转变。3) 建议构建涵盖材料类型、界面结构、力学性能、多场响应的跨尺度协同机制图谱,将离散实验数据系统集成,形成可解释、可推演的理论模型体系,推动界面性能的定量化预测。4) 人工智能与机器学习方法的引入将为界面研究提供全新解耦与优化路径。在已有实验或模拟数据基础上,可借助监督学习、图神经网络、强化学习等策略,构建面向界面性能预测、增强机制识别与设计参数优化的智能模型。通过 AI 工具对影响界面性能的多因素进行特征抽取与权重评估,有望实现界面性能的定量设计,显著缩短试验周期与优化时间。在应用方面,未来应聚焦典型工程场景,开展界面增强技术的集成设计与工程验证。特别是在 3D 打印混凝土、再生混凝土、既有结构修复、界面修补、界面疲劳防护、自愈合界面等方向,纳米填料的结构调控与智能响应潜力尤为突出。

综上所述,纳米水泥基复合材料黏结性能与结合界面特征研究正处于由现象认识迈向机制解析与设计控制的阶段。通过发展高分辨表征技术、构建多尺度理论模型、引入智能优化方法并面向工程实践转化,基于界面纳米填料改性设计有望为水泥基材料及其结构物的高性能、多功能与长寿命提供坚实支撑。

4 结论

纳米科学与技术的迅速发展为改善水泥基复合材料的黏结性能与结合界面特征提供了新的思路与手段。通过纳米填料改性,可增强界面致密性、提升黏结强度、抑制界面微裂纹萌生与扩展,从而实现水泥石-骨料、水泥砂浆-骨料、新-旧水泥基材料及水泥基材料-增强筋等多种界面的黏结性能提升。当前的研究已初步揭示纳米填料在界面区的富集行为与纳米中心效应,为构建高力学、高耐久性的水泥基材料及其结构物奠定了理论基础。然而,界面区域的多尺度表征、纳米改性机制的定量化描述及长期服役下的界面演化规律仍是亟须突破的关键问题。

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韩宝国: 提出核心构想、指导整体框架和逻辑、修订论文

Research Progress on Interfaces inside Nanofiller-Modified Cement-Based Materials and Their Structures

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Extended Abstract

The interfaces in cement-based materials and their structures (*i.e.*, the cement paste-aggregate, mortar-aggregate, new-to-old concrete, and reinforcement-concrete interfaces) are widely recognized as the most critical and weakest zone governing overall mechanical properties and durability. Under the combined influence of wall, one-sided growth, and bleeding effects, these interfaces are typically characterized by high porosity, elevated calcium hydroxide (CH) crystal content, and a high degree of hydration, resulting in intrinsically low hardness and strength. As a result, cracks initiate, propagate, and interconnect within the interfaces under loading, leading to a macroscopic failure. Meanwhile, their loose and porous structure facilitates the ingress of water and harmful ions, reducing durability and accelerating deterioration.

For the pronounced multi-scale nature of cement-based materials, modifying microstructure in nanoscale provides an effective “bottom-up” approach to improving interfacial bond and overall performance. Compared with conventional top-down methods, this strategy exhibits effective modification for different types of interfaces. With the rapid development of nanotechnology, incorporating nanofillers demonstrates a great potential in interfacial modification. This review represents the effects and underlying mechanisms of nanofillers on the interfaces in cement-based materials and their structures, as well as discusses key challenges and future research directions.

Adding nanofillers can significantly enhance the bond performance of various interfaces in cement-based materials and their structures. The experimental studies show that the incorporation of nanofillers can increase the bond strength of cement paste-aggregate and mortar-aggregate interfaces by 65.3% and 42.8%, respectively. Also, nanofillers effectively enhance the bond of new-to-old cement-based materials, increasing interfacial strength by 39.0%. Their beneficial effects are evident in the interfaces between reinforcements and cement-based materials, where the addition of nanofillers improves bond strength and reduces slip behavior. These modifications contribute to a high stress transfer efficiency, as well as better load-bearing capacity and structural stability. The enhancement efficiency is closely related to the geometric dimensionality of nanofillers, generally following an order, *i.e.*, two-dimensional (2D) > one-dimensional (1D) > zero-dimensional (0D).

The improved bond performance derives from the modified interfacial characteristics. Key effects include increased compactness, reduced porosity, refined CH crystal size, and decreased interfacial thickness. For instance, the thickness of the interfacial transition zone can be reduced from approximately 50 μm to 10 μm or less after nanomodification, as reflected by the reduced porosity and altered Ca/Si ratio of calcium silicate hydrate (C-S-H) gels. Meanwhile, nanofillers also suppress the formation and growth of large CH crystals, replacing them with finer and more uniformly distributed hydration products. Micromechanical characterization techniques such as nanoindentation and atomic force microscopy reveal significant increases in elastic modulus and hardness in the interfacial zone, indicating that new hydration products like superhard C-S-H gels induced by nanomodification are formed.

The mechanisms underlying nanofiller-induced interfacial modification can be categorized into two key aspects, *i.e.*, the enrichment effect and the nano-core effect. The enrichment effect arises from the preferential accumulation of nanofillers in the interfacial region due to the wall effect, capillary-driven migration, and gravity effect. This leads to a higher local concentration of nanofillers, providing abundant nucleation sites for hydration products. The nano-core effect, which builds upon the intrinsic properties of nanofillers, involves several specific mechanisms, *i.e.*, (1) Adsorption effect: Nanofillers adsorb cations such as Ca^{2+} and Mg^{2+} , promoting the nucleation of C-S-H and leading to the formation of nano-core-shell elements. These structures inhibit the oriented growth of CH crystals and enhance interfacial densification; (2) Filling effect: Nanofillers fill interfacial pores through the formation of nano-core-shell elements, improving packing density and reducing porosity; (3) Short-range and long-range effect: Nanofillers can modify the nanostructure and properties of hydration products in a short range, and refine and optimize the hydration products near nanofillers in a long range; (4) Pozzolan effect: Reactive nanofillers, such as nano-silica, react with CH to generate additional C-S-H, refining the microstructure and improving bonding; (5) Thermal conductivity effect: High-conductivity nanomaterials (*e.g.*, carbon nanotubes, graphene) homogenize the temperature distribution during hydration, reducing thermal stress and early-age cracking; (6) Self-curing effect: Hydrophilic nanomaterials, such as nanocellulose, absorb and release water, mitigating early-age shrinkage and enhancing microstructural development; and (7) Pinning and bridging effects: Nanofillers inhibit crack initiation and propagation (pinning effect) and bridge microcracks (bridging effect), thereby improving interfacial toughness and strength.

Summary and prospects Despite significant achievements, several challenges remain in understanding and optimizing nanofiller-modified interfaces. First, the existing characterization techniques are limited in their ability to capture the dynamic evolution of interfacial structures at high spatial and temporal resolution. Most methods provide only static, two-dimensional information, making it difficult to fully understand multi-scale and multi-physics processes. Second, the inherent heterogeneity and discontinuity of interfaces complicate quantitative modeling. The existing models often describe average behavior, but fail to capture local weak zones or nanoscale force transfer mechanisms. Third, the introduction of multifunctional nanofillers increases the complexity of multi-field coupling (*i.e.*, mechanical, thermal, chemical, and electrical), posing challenges for unified theoretical frameworks. Finally, the large-scale engineering application of nanomodified interfaces is hindered by some issues such as nanofiller dispersion, cost, and performance stability under complex service conditions.

Future research should focus on several key directions. Advanced characterization techniques with a high spatiotemporal resolution, such as synchrotron radiation-based imaging and X-ray computed tomography, should be developed to enable real-time tracking of interfacial evolution. The integration of artificial intelligence and machine learning can facilitate high-throughput data analysis and predictive modeling, enabling a quantitative design of interfacial properties. Multi-scale theoretical frameworks that link material composition, microstructure, and macroscopic performance are needed to achieve accurate prediction and optimization. Also, efforts should be made to translate laboratory findings into practical engineering applications, particularly in emerging areas such as 3D-printed concrete, recycled concrete, concrete repair, and self-healing cement-based materials.

In summary, nanomodification is demonstrated to effectively tailor interfaces in cement-based materials and their structures, while the enrichment effect and nano-core effect is proposed to clarify the underlying mechanisms. These advances provide a foundation for mitigating the inherent weakness of interfaces. Despite these advances, some challenges remain in terms of characterization, quantitative modeling, and large-scale application. Nevertheless, continued progress in nanotechnology, multi-scale analysis, and intelligent design is expected to enable the rational design and engineering of high-performance, durable, and multifunctional cement-based materials and their structures.

Keywords nanofillers; cement-based materials and their structures; interfacial properties; interfacial characteristics; modification mechanisms