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金刚石增强复合材料的声制造形性调控研究

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Research on Acoustic Manufacturing for Structural and  
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## 摘要

金刚石增强复合材料凭借其卓越的热力学性能，已成为电子信息、智能机器人和高端医疗等领域的新一代先进材料。然而，无论是陶瓷、金属还是树脂基体系，这类由异质组元构成的复合材料普遍存在界面结合问题，界面的不连续性严重制约了其综合性能的充分发挥；同时，现有制造技术受限于能场灵活性，难以实现复杂形状与梯度性能的精准调控，极大制约了金刚石复合材料在柔性传感领域等多样化场景中的应用。为此，本团队开创性提出了一种利用超声进行直接制造的原创“声制造”法，其突破了传统制造技术局限，具备 360°全方位成型和性能连续可调特点。然而，目前声制造法的性能调控范围仍无法满足高灵敏度力传感应用对材料梯度化特性的特殊需求；将金刚石作为增强相引入其中时，其对梯度性能调控的影响机制尚未明确；声波对复合材料的界面形成和成型作用机制也并不清楚。因此，深入研究以上基础机制，是实现金刚石增强复合材料定点定量声制造形性调控的关键，对发展一种以声波为精确控制能场的高性能器件制造方法，并推动其在柔性传感这一全新领域的创新应用具有重要意义。

本文在 XXX 项目的支持下，首次提出采用原创声制造法，快速制造具备多种可控形性特征的金刚石增强复合材料。系统研究金刚石与陶瓷、金属和树脂基体间的界面结构和组分特性，探明不同能场下复合材料的界面形成机理与相互作用关系；从微观、介观和宏观尺度出发，深入研究声场下金刚石颗粒对材料的声化学、机械及物理效应的增强机制，揭示声制造金刚石增强复合材料形性调控的关键作用机制；掌握系列点-线-面-体结构的多向梯度性能精准调控方法，建立定点定量形性调控的声制造工艺体系；探明声制造梯度性能结构的传感机理，创新设计系列柔性传感器。主要结论如下：

(1) 探明了不同能场下金刚石和陶瓷、金属和树脂等基体的界面结构、组分特性以及界面结合模式，揭示了其界面形成机理和相互作用关系。针对金刚石氮化硅陶瓷基复合材料，发现在温度和压力场（热压场）作用下，Ti 镀层的引入促使界面形成了以  $\text{TiC}_i\text{N}_{1-i}$  为过渡层的化学结合界面，过渡层作为界面“桥梁”，降低了传热中的声子振动失配，并抑制了金刚石石墨化，形成了连续界面结构；针对金刚石金属基复合材料，在热流场作用下，金属玻璃（BMG）基体内部的多尺度原子团簇发生迁移，促使金刚石快速嵌入处于塑性流动的基体中，形成紧密结合界面。Ti 镀层的引入促进了溶

解-扩散界面的形成，增大了结合界面面积并形成微机械互锁界面。但这类界面结合模式仅为次价键结合，尚未形成结合力更强的化学结合界面。

(2) 进一步地，采用声波进行界面强化，发现在声场下金刚石表面活性官能团与树脂基体间形成了化学锚定连接，声波的局部能量促使金刚石表面的活性羟基与树脂基体分子的硅氢键发生脱氢反应形成硅氧键，形成了薄而高度分散的硅氧化物界面层，构建了连续稳定的化学键合界面，其界面强度远高于常规热能场下的机械嵌合界面（提升 375 %）。这种非接触式声场的独特优势，为金刚石增强复合材料实现精准、可控的界面优化提供了新思路。

(3) 基于声场下金刚石/树脂的界面键合机理，提出采用声制造法快速制造金刚石/树脂复合材料，并探究其在微观、介观和宏观尺度上的关键作用机制。发现在声制造成型中，材料体系呈现出显著的声化学、机械和物理等三种声学效应。微观尺度上，主要表现为声化学和机械效应：声化学效应主要源于声波产生的极端热力学条件，这种特殊环境促使材料形成活性自由基群，进而迅速引发化学聚合反应和交联网络形成；声机械效应则通过超声传播产生的周期性振动驱动分子链化学键的断裂与重组，从而强化材料的聚合程度和交联网络密度。介观尺度上，则以声物理效应为主，其主要表现为声空化行为：声波诱发的周期性压力变化促使树脂体系产生大量空化气泡，这些气泡的持续产生与溃灭为材料提供了初始活化能，从而诱导材料固化成型。

(4) 而金刚石颗粒的引入显著强化了不同尺度下的声化学、机械和物理效应。微观尺度上，声波于金刚石颗粒表面的强烈超声冲击波，促使颗粒表面活性羟基断裂，形成更高含量的活性自由基，声化学效应的强化有效提升了聚合与交联程度（反应性官能团（如乙烯基）调控范围较纯树脂体系提高了 26.32 %）。同时，金刚石颗粒的引入改变了声场动量分布，通过声波与颗粒相互作用实现了声机械力的空间均匀分散。这种声机械效应的增强，促进了分子链运动与碰撞，大幅提升了微观分子聚合程度（强化效果约为纯树脂体系的两倍）。介观尺度上，金刚石颗粒的加入还增强了声空化行为。一方面，金刚石作为异质增强颗粒，为空化气泡提供了多重成核位点，加剧了空化效应并增强其分布均匀性；另一方面，金刚石的存在还降低了气泡形核能垒，促进了更频繁的气泡成核、生长和坍塌循环，更有利于气泡持续释放能量，加速了局部固化速率。

(5) 宏观尺度上, 三种声学效应的协同作用实现了金刚石/树脂复合材料由点到面的逐级连续成型: 即声化学效应持续驱动聚合交联反应(微观固化根本机制)、声机械效应强化聚合交联网络(微观强化作用)、声物理效应通过气泡坍塌产生的瞬时高温高压实现了局部固化成型(介观成型作用)。这三种声学效应协同作用最终实现了金刚石/树脂复合材料从微观分子聚合到宏观结构的连续声制造成型。

(6) 基于上述声制造成型的关键作用机制, 进一步探究金刚石/树脂复合材料的声制造形性调控方法, 开展系列“点-线-面-体”结构的多向梯度性能精准调控研究。针对“点”状结构, 发现金刚石颗粒通过协同增强声化学、机械和物理效应, 显著提升了声波对微观结构的调控能力(反应性官能团(如乙烯基)转化率的调控范围较纯树脂体系提升了 56.67 %, 交联密度的调控范围增幅达 98.05 %)。利用声波将梯度结构可控的“点”连接成“线”, 再编织成“面”时, 梯度结构设计使材料受力时能够更灵活地适应形变, 实现了应力分布与能量吸收的动态调节, 拉伸强度较均质结构提升 30.07%。特别地, 声波于三维空间的可控调节, 还可构建具有多向梯度弹性的“体”结构, 在不同空间维度(横、纵及环向)上实现了弹性模量的可控分布, 这种梯度性能结构表现出显著的空间力学响应特性, 为微小力的快速响应和灵敏感知提供了可能。

(7) 基于上述梯度性能结构调控特性, 设计并制造适用于不同应变、压力和触觉感知的柔性传感器。利用梯度性能“面”编织体优异的外部形变适应力, 设计并制造了适用于快速应变传感的柔性应变传感器, 灵敏度达 54.94, 较均一性能传感器提升了 60.46%, 较纯树脂功能层传感器提升 43.89 %, 实现了人体关节活动的实时监测; 利用横向梯度性能“体”微结构在受力时出现的多层次变形, 制造了适用于微细压力或振动传感的柔性压力传感器, 实现了人体微细动作、生命体征、微细力或振动的精确监测; 此外, 基于环向梯度性能指纹结构由内至外的差异化力学响应, 其在微小载荷下即可产生强信号变化, 所设计的指尖触觉传感器具备高灵敏度 ( $0.493 \text{ kPa}^{-1}$ ) 和响应速度 ( $65.19 \text{ ms}$ ), 响应速度近乎常规传感器两倍, 可精准识别表面粗糙度和精细纹理结构。

**关键词:** 金刚石增强复合材料; 声制造; 界面优化; 形性调控; 柔性传感器

## ABSTRACT

Diamond reinforced composite materials, with their excellent thermodynamic properties, have become a new generation of advanced materials in fields such as electronics, intelligent robots, and high-end healthcare. However, whether in ceramic, metallic, or resin-based systems, these composites composed of heterogeneous components commonly suffer from interfacial bonding issues. The discontinuity at the interface severely restricts the full utilization of their comprehensive performance. Additionally, existing manufacturing technologies are constrained by limited flexibility in shaping, making it difficult to directly fabricate diamond composites with complex shapes and continuously adjustable gradient properties. This greatly restricts the application of diamond reinforced composites in diverse scenarios, such as flexible sensing. To address these challenges, our team has innovatively proposed an original "acoustic manufacturing" method that utilizes ultrasound for direct manufacturing. This method overcomes the limitations of conventional techniques, enabling 360° omnidirectional forming and continuously adjustable properties. Nevertheless, the current performance control range of acoustic manufacturing method is still unable to meet the special requirements of high-sensitivity force-sensing applications for gradient material properties. When diamond is introduced as a reinforcing phase, the mechanism of its influence on the regulation of gradient performance is not clear. The mechanism of acoustic wave on the interface formation and forming of composite materials is also unclear. Therefore, in-depth research into these fundamental mechanisms is crucial for achieving fixed-point quantitative structural and performance control of acoustic manufacturing diamond-reinforced composites. This is of great significance for developing a high-performance device manufacturing method that employs acoustic waves as a precisely controllable energy field, and promoting its innovative application in the new field of flexible sensing.

Supported by the XXX Project, this study proposes, for the first time, an original acoustic manufacturing method to rapidly fabricate diamond-reinforced composites with multiple controllable structural and functional properties. The research systematically investigated the interfacial structures and compositional characteristics between diamond and ceramic, metal, and resin matrix. It elucidated the interfacial formation mechanisms and interaction relationships of composites under different energy fields. From micro-, meso-, to macro-scales, the study thoroughly examined the enhancement mechanisms of the acoustic chemical, mechanical, and physical effects of diamond particles on materials under acoustic fields, revealing the key mechanism of structure-performance control in acoustic manufacturing.

Furthermore, it developed precise multi-directional gradient property control methods for point-line-plane-volume structures, establishing an acoustic manufacturing process system for targeted and quantitative structure-performance control. Additionally, the study clarified the sensing mechanisms of gradient-performance structures fabricated via acoustic manufacturing and innovatively designed a series of flexible sensors. The main findings are as follows:

(1) Under different energy fields, the interfaces between diamond and ceramic, metal, and resin matrices exhibited different structural characteristics and interaction relationships. For diamond  $\text{Si}_3\text{N}_4$  ceramic matrix composite materials, an interfacial transition layer ( $\text{TiC}_i\text{N}_{1-i}$ ) was formed between diamond and ceramic matrix due to the introduction of Ti coating under thermal pressure field. This layer served as an interface "bridge", reducing phonon vibration mismatch in heat transfer, suppressing diamond graphitization, and establishing a continuous interface structure; For diamond metal matrix composites, the multi-scale atomic clusters in metal glass (BMG) matrix migrated under the thermal flow field, enabling rapid embedding of diamond particles into the plastically flowing matrix, forming a tightly bonding interface. The introduction of interfacial coatings promoted the formation of a dissolution-diffusion interface, increased the bonding interface area, and created a micro mechanical interlocking interface. However, this bonding mode remained limited to secondary bonds, and has yet to achieve stronger chemical bonding.

(2) Furthermore, by using acoustic waves for interface strengthening, it was found that chemical anchoring connections were formed between the active functional groups on the diamond surface and the resin matrix under the acoustic field. The localized energy of acoustic waves induced a dehydrogenation reaction between the hydroxyl groups on the diamond surface and the Si-H bonds of the resin matrix. This process created a thin, highly dispersed Si-O interfacial layer, establishing a continuous and stable chemical bonding interface. The interfacial strength of this bond was significantly higher than that of mechanical interlocking interface formed under conventional thermal fields (an increase of 375%). The unique advantages of this non-contact acoustic field offer a novel strategy for achieving precise and controllable interface optimization in diamond-reinforced composites.

(3) Based on the interfacial bonding mechanism of diamond/resin under acoustic fields, this study proposed an acoustic manufacturing method for the rapid fabrication of diamond/resin composites, and investigated their key mechanisms at micro-, meso-, and macro-scales. It was found that in acoustic manufacturing, the material system exhibited three

distinct acoustic effects: acoustic chemical, mechanical, and physical effects. At the microscopic scale, acoustic chemical and mechanical effects were predominant: acoustic chemical effects are mainly caused by the extreme thermodynamic conditions generated by acoustic waves. This special environment promoted the formation of active free radical groups in materials, rapidly triggering chemical polymerization and cross-linking network formation; The mechanical effect, driven by periodic ultrasonic vibrations, facilitated the breakage and recombination of molecular chain bonds, thereby enhancing polymerization efficiency and crosslinking density. At the mesoscopic scale, the acoustic physical effect was dominant, primarily manifesting as acoustic cavitation: the periodic pressure changes induced by acoustic waves promoted the generation of a large number of cavitation bubbles in the resin system. The continuous formation and collapse of these bubbles provided initial activation energy for the material, thus promoting curing.

(4) The introduction of diamond particles was found to significantly enhance the acoustic chemical, mechanical, and physical effects at different scales. At the microscopic scale, the intense ultrasonic shockwaves generated by acoustic waves at the diamond particle surfaces promoted the breakage of active hydroxyl groups, forming a higher content of reactive free radicals. This intensified acoustic chemical effect effectively improved polymerization and crosslinking efficiency, with the controllable range of reactive functional groups (e.g., vinyl groups) expanding by 68.94% compared to pure resin systems. Simultaneously, the introduction of diamond particles altered the acoustic momentum distribution, achieving spatially uniform dispersion of acoustic mechanical forces through the interaction between acoustic waves and particles. This enhanced acoustic mechanical effect facilitated molecular chain movement and collision, greatly improving micro molecular polymerization (about twice that of pure resin systems). At the mesoscopic scale, diamond particles further amplified acoustic cavitation behavior. Functioning as heterogeneous nucleation sites, they not only intensified cavitation effects and improved distribution uniformity but also reduced the energy barrier for bubble nucleation. This dual effect promoted more frequent cycles of bubble nucleation, growth, and collapse, with sustained energy release accelerating local curing rates.

(5) At the macroscopic scale, the synergistic interaction of these three acoustic effects enabled the progressive and continuous curing of diamond/resin composites from localized points to full-area integration. Specifically, the acoustic chemical effect continuously drove polymerization and crosslinking reactions (serving as the fundamental microscopic curing mechanism), while the mechanical acoustic effect reinforced the polymerization-crosslinking

network (micro strengthening effect). Concurrently, the physical acoustic effect facilitated local curing through transient high-temperature/pressure conditions generated by cavitation bubble collapse (mesoscopic curing effect). The synergistic effect of these three acoustic effects ultimately achieved continuous acoustic manufacturing of diamond/resin composite materials from micro molecular polymerization to macro structure.

(6) Based on the above mechanism of acoustic manufacturing, this study further investigated the structure-performance control methods of acoustic manufacturing diamond/resin composite materials, systematically exploring the precise control of multidirectional gradient performance in "point-line- plane -volume" structures. For "point" structures, diamond particles were found to significantly enhance the acoustic regulation capability of microstructures through synergistic reinforcement of acoustic chemical, mechanical, and physical effects. The regulation range of the conversion rate of reactive functional groups (such as vinyl) has increased by 56.67 % compared to pure resin systems, and the regulation range of crosslinking density has increased by 98.05 %. When connecting the gradient structure controllable "points" into "lines" and weaving them into "plane", the gradient structure design enabled the material to adapt more flexibly to deformation under stress, achieving dynamic adjustment of stress distribution and energy absorption. The tensile strength was increased by 30.07 % compared to homogeneous structures. Notably, three-dimensional acoustic modulation could further construct "volume" structures with multidirectional gradient elasticity, realizing controllable elastic modulus distribution across different spatial dimensions (transverse, longitudinal, and circumferential). This gradient performance structure exhibited significant spatial mechanical response characteristics, providing the possibility for rapid response and sensitive perception of minute forces.

(7) Based on the gradient performance structure control characteristics described above, a series of flexible strain, pressure, and tactile sensors were designed and fabricated. By utilizing the enhanced external deformation adaptability of gradient "plane" woven structures, a flexible strain sensor for rapid strain sensing was developed. Its sensitivity reaches 54.94, which is 60.46 % higher than that of a uniform performance sensor, and enabling real-time monitoring of human joint activity. The multi-level deformation exhibited by transverse gradient performance "volume" microstructure arrays under load was employed to fabricate flexible pressure sensors suitable for detecting subtle motions, vital signs, and micro-forces or vibrations. Furthermore, the circumferential gradient performance fingerprint structures demonstrated strong signal variation under minimal loading due to their radially differentiated

mechanical response. The designed fingertip tactile sensor exhibited improved wearability, sensitivity ( $0.493 \text{ kPa}^{-1}$ ), and response speed (65.19 ms), with a response speed almost twice that of conventional sensors, and can accurately identify surface roughness and fine texture structures.

**Key words:** Diamond-reinforced composites; Acoustic manufacturing; Interface optimization; Structure-performance control; Flexible sensors