

Functionally Graded Materials for Variable Thermal Environments

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Abstract

Engineering components exposed to variable thermal environments must withstand spatial temperature gradients, repeated heating and cooling, thermally induced strain, oxidation, and mismatch between materials selected for structural and thermal functions. Conventional homogeneous materials frequently require compromises between thermal resistance, mechanical strength, thermal conductivity, density, and fracture resistance, whereas abrupt multimaterial joints can generate severe interfacial stresses because adjoining constituents possess different coefficients of thermal expansion and elastic properties. Functionally graded materials offer an alternative architecture in which composition, microstructure, porosity, or another material parameter varies gradually through a selected spatial direction, thereby producing corresponding gradients in thermal and mechanical properties.

This study develops a simulation-based framework for designing functionally graded materials intended for variable thermal environments. Because authenticated thermal-cycle experiments, microstructural measurements, thermophysical property maps, and finite-element data were not supplied, all quantitative results are explicitly synthetic. A metal–ceramic thermostructural system is modeled across through-thickness temperature differences from 100 to 700 °C and compared in three architectures: an abrupt bi-material interface, a linear functional gradient, and an optimized nonlinear functional gradient. A Variable Thermal Environment Grading Index is proposed using thermal-expansion compatibility, conductivity tailoring, elastic-modulus continuity, gradient smoothness, high-temperature phase stability, and manufacturing fidelity. Simulated results show that at a 500 °C temperature difference, peak thermal stress reaches 812 MPa for the abrupt bi-material system, 592 MPa for the linear gradient, and 469 MPa for the optimized nonlinear gradient.

The corresponding reduction of approximately 42.2% relative to the abrupt interface illustrates the potential value of tailoring the spatial property profile rather than merely joining two high-performance constituents. The analysis also demonstrates that an excessively steep gradient can recreate local stress concentration and that thermal optimization must therefore consider both heat-transfer and mechanical-response objectives.

Keywords: functionally graded materials, thermal stress, variable thermal environments, thermal barrier materials, metal–ceramic gradients, thermal shock, thermomechanical design, additive manufacturing.

1. Introduction

Engineering components used in propulsion systems, energy-conversion equipment, heat exchangers, thermal-protection structures, combustion hardware, electronic devices, and other temperature-sensitive applications experience environments in which temperature changes spatially and temporally. A surface may be subjected to severe heating while the opposite side remains comparatively cool, or the entire component may repeatedly transition between high and low temperatures. These gradients produce constrained thermal expansion and corresponding thermal stresses. Traditional material selection is difficult because materials capable of resisting severe heat, such as engineering ceramics, can possess comparatively low fracture toughness, while metals offering ductility and structural integrity may have lower temperature resistance. The original development of functionally graded materials was closely connected with this thermal-barrier problem: Koizumi described the concept as a means of introducing continuous variations in composition, microstructure, and properties so that heat resistance and structural functionality could coexist without a severe abrupt interface.

The central feature of a functionally graded material is spatial variation. Instead of maintaining a constant material composition throughout the component or placing two materials together at one discrete boundary, the constituent volume fractions vary gradually. A ceramic-rich region may therefore face the high-temperature environment, while the material transitions progressively toward a metal-rich structural region. Because thermal conductivity, coefficient of thermal expansion, elastic modulus, strength, and other properties vary with composition, their effective values also change through the graded direction. Classical thermomechanical analyses demonstrated that material-distribution functions have a strong influence on the displacement, stress, and thermal response of graded plates and structures. Reddy's plate formulation, for example, incorporated thermomechanical coupling and spatially varying effective properties, establishing a widely used theoretical foundation for the analysis of graded structures.

The reduction of thermal stress is nevertheless not automatic. Noda's analysis of thermal stresses in functionally graded systems emphasized that severe thermal loading can still generate high stresses and crack-driving forces and that the spatial composition profile should therefore be optimized rather than treated simply as a gradual mixture. Thermal shock adds a further challenge because cracks can initiate from the ceramic-rich surface or from regions in which thermal and mechanical properties change rapidly. Research on graded materials containing cracks has shown that thermal-shock resistance is influenced by both stress magnitude and fracture-mechanics parameters, meaning that a gradient producing low average thermal stress may still contain a critical local region.

Manufacturing capability has expanded the design space available for these materials. Earlier processing routes included powder metallurgy, centrifugal methods, thermal spraying, vapor deposition, and sintering-based techniques. More recent additive manufacturing approaches can vary feedstock composition spatially and create metal-metal, metal-ceramic, and metal-intermetallic gradients within complex three-dimensional components. Ghanavati and Naffakh-Moosavy's review documents how additive manufacturing enables controlled variation of chemistry and microstructure but also introduces challenges involving melting, solidification, residual stress, phase formation, and process control. Reviews of functionally graded additive manufacturing further emphasize that gradient design should

occur across multiple scales, from overall component geometry to material composition and microstructure.

The present study develops a methodological framework for designing Functionally Graded Materials for Variable Thermal Environments. Rather than asking whether a graded material is generally superior to a homogeneous system, the research asks how the spatial property gradient should change when thermal severity changes. A synthetic metal–ceramic system is evaluated under multiple through-thickness temperature differences and three material architectures. Particular attention is directed toward peak thermal stress, interfacial compatibility, thermal conductivity, effective expansion behavior, and gradient manufacturability. Because no experimental dataset was supplied, the numerical component is explicitly simulation based and is intended to establish an analytical structure for later verification using real finite-element, thermal-cycle, microscopy, and mechanical-test data.

2. Objectives of the Study

2.1 Development of a Variable-Thermal-Environment Grading Framework

The first objective is to develop a material-design framework in which the functional gradient is directly related to the anticipated thermal environment. A component exposed to a relatively small temperature difference does not necessarily require the same compositional profile as one exposed to severe thermal gradients. The gradient should therefore respond to the severity, direction, and duration of thermal loading rather than remain a fixed manufacturing prescription.

The framework combines heat-transfer requirements with thermal-expansion compatibility and structural performance. The ceramic-rich region is intended to provide thermal resistance, while the metal-rich region provides toughness and load-carrying capability. Intermediate material fractions are selected to reduce abrupt property discontinuities and distribute thermal mismatch over a larger volume.

2.2 Evaluation of Gradient Shape and Peak Thermal Stress

The second objective is to compare abrupt, linear, and optimized nonlinear transitions. A linear gradient is simple to describe and manufacture, but the optimal spatial variation in material properties does not necessarily follow a linear function. Thermal conductivity, elastic modulus, and thermal expansion can respond nonlinearly to constituent fraction and temperature.

Accordingly, the study examines whether a tailored nonlinear gradient can reduce peak thermal stress more effectively than a linear transition. The primary interest is not merely the magnitude of average stress but the location and magnitude of the maximum thermomechanical stress capable of initiating cracking or local failure.

2.3 Assessment of Manufacturability and Thermal-Structural Robustness

The third objective is to ensure that theoretically favorable gradients remain physically manufacturable. Very rapid local changes in feedstock composition can produce undesirable phases, porosity, residual stress, incomplete bonding, or chemical incompatibility during fabrication.

The proposed framework therefore includes manufacturing fidelity, phase stability, gradient smoothness, and high-temperature material compatibility alongside thermal-stress performance. This

prevents numerical optimization from generating a mathematical composition profile that cannot be reproduced reliably in an actual component.

3. Review of Literature

3.1 Functional Gradation for Thermal Stress Mitigation

Functionally graded materials were developed largely in response to severe thermomechanical mismatch in high-temperature systems. Koizumi's historical account describes the early Japanese development program in which continuous compositional and microstructural changes were used to create gradients in properties such as thermal conductivity and mechanical strength. The program specifically targeted thermal-stress relaxation in components intended for severe thermal environments.

Noda subsequently provided an extensive treatment of thermal stresses in functionally graded materials and demonstrated why spatial composition should be optimized under severe thermal loading. Thermal stress is created not simply by temperature difference but by the combination of temperature distribution, constraint, elastic response, and thermal-expansion mismatch. A ceramic and a metal may each possess suitable individual properties but generate severe stress when directly bonded because they attempt to expand by different amounts.

3.2 Thermomechanical Modeling of Graded Structures

Thermomechanical analysis of FGMs has developed through analytical, semi-analytical, and finite-element formulations. Reddy and Chin analyzed thermomechanical response in graded plates and cylinders, while Reddy's subsequent plate formulation incorporated material variation, thermomechanical coupling, geometric nonlinearity, and time dependency. Reddy and Cheng later provided three-dimensional thermomechanical solutions for graded rectangular plates, demonstrating that through-thickness stress and displacement fields can differ substantially from assumptions made in simplified homogeneous plate theories.

The simplicity of the power-law model makes it useful for analysis, but it does not imply that one power-law exponent is optimal for every thermomechanical objective. The gradient exponent can redistribute stiffness and expansion in ways that reduce stress at one location while increasing it elsewhere. Consequently, variable thermal environments require optimization across the complete thermal field rather than selection of an arbitrary exponent.

3.3 Manufacturing Evolution and Gradient Fidelity

Processing technology determines how closely the manufactured material follows the intended gradient. Modern reviews identify powder metallurgy, centrifugal casting, thermal spraying, deposition, and additive manufacturing among the principal routes used to fabricate graded materials. Sam, Jojith, and Radhika emphasize that manufacturing method, thermal treatment, residual stress, gradation control, and coating precision are closely connected with final FGM performance.

Additive manufacturing is particularly significant because material composition can be changed during deposition. Ghanavati and Naffakh-Moosavy describe experimental and numerical development of metal-metal, metal-ceramic, and metal-intermetallic graded systems and emphasize the importance of melting, solidification, microstructure, and process simulation. Reichardt and colleagues likewise

identify additive manufacturing as a route for producing metal-based FGMs with spatially controlled chemistry and microstructure.

However, additive manufacturing introduces its own limitations. Rapidly changing material composition may cause cracking, undesirable intermediate phases, thermal-expansion mismatch during deposition, composition dilution, lack of fusion, or unstable melt-pool behavior. The theoretical gradient must therefore be filtered through a manufacturability constraint. The best functional gradient is not the mathematically smoothest distribution but the smoothest thermally effective profile that can be repeatedly fabricated with acceptable defects and phase stability.

4. Research Methodology

4.1 Research Design and Synthetic Thermostructural System

The study adopts a simulation-based thermomechanical design. No fabricated FGM specimens, thermocouple histories, thermal conductivity measurements, microstructural maps, residual-stress data, or thermal-shock tests were supplied. All numerical values are therefore synthetic and used exclusively to demonstrate the proposed methodology.

A generic metal–ceramic component with normalized thickness h is modeled. The hot surface is ceramic rich to provide thermal resistance, while the opposite surface is metal rich to retain ductility and structural support.

Table 1: Thermomechanical Variables Used in the FGM Design Framework

Design Variable	Proposed Experimental/Computational Evidence	Function in Thermal Design	Principal Risk if Poorly Controlled
Thermal conductivity gradient	Laser-flash diffusivity, conductivity testing, thermal simulation	Controls temperature penetration through thickness	Excessive local temperature gradients
Coefficient of thermal expansion	Dilatometry across compositions	Controls mismatch strain	Interfacial or local tensile stress
Elastic modulus distribution	High-temperature mechanical testing or nanoindentation	Controls stress redistribution	Excessive stiffness concentration
Gradient smoothness	SEM/EDS composition profile or CT-based phase mapping	Distributes material mismatch	Local property discontinuity
High-temperature phase stability	XRD, DSC/TGA, microscopy	Preserves designed properties during service	Reaction layers or phase degradation

Design Variable	Proposed Experimental/Computational Evidence	Function in Thermal Design	Principal Risk if Poorly Controlled
Manufacturing fidelity	Composition map versus prescribed profile	Determines whether numerical gradient exists physically	Loss of predicted stress benefit

4.2 Variable Thermal Environment Grading Index

Thermal-expansion compatibility receives the largest individual weight because mismatch strain is a major driver of thermal stress. Thermal conductivity and elastic modulus each receive substantial weight because they determine the temperature field and conversion of thermal strain into stress.

VTEGI ranges from 0 to 1. A higher score represents a material architecture whose thermal and mechanical gradients are better coordinated with the expected environment.

4.3 Thermomechanical Modeling and Gradient Optimization

where $\sigma_{\max}$ is maximum thermally induced stress, q_{hot} represents heat-flow exposure or another thermal-performance metric, and $G_{\text{manufacturing}}$ penalizes gradients too steep to fabricate reliably.

The formulation deliberately prevents the optimization process from reducing stress by simply eliminating the ceramic-rich thermal barrier. Hot-side thermal protection remains a boundary requirement.

5. Analysis

5.1 Thermal Stress Under Increasing Temperature Difference

The synthetic analysis indicates that all material systems experience increasing thermal stress as the temperature difference becomes more severe. The abrupt bi-material architecture exhibits the strongest increase because the coefficient of thermal expansion and elastic stiffness change sharply at one interface.

- At a temperature difference of 100 °C, the abrupt system reaches a simulated peak thermal stress of 145 MPa. The linear FGM reduces this value to 112 MPa, while the nonlinear optimized FGM records 91 MPa.
- The difference becomes substantially more important as thermal severity increases. At $\Delta T=500^{\circ}\text{C}$, the abrupt interface reaches 812 MPa. The linear graded system records 592 MPa, whereas the nonlinear architecture reduces the peak value to 469 MPa.
- At the most severe modeled condition, the abrupt architecture reaches 1,205 MPa compared with 868 MPa for the linear gradient and 688 MPa for the nonlinear design.

These results illustrate that material architecture becomes increasingly consequential as thermal mismatch grows.

5.2 Comparative Performance of Material Architectures

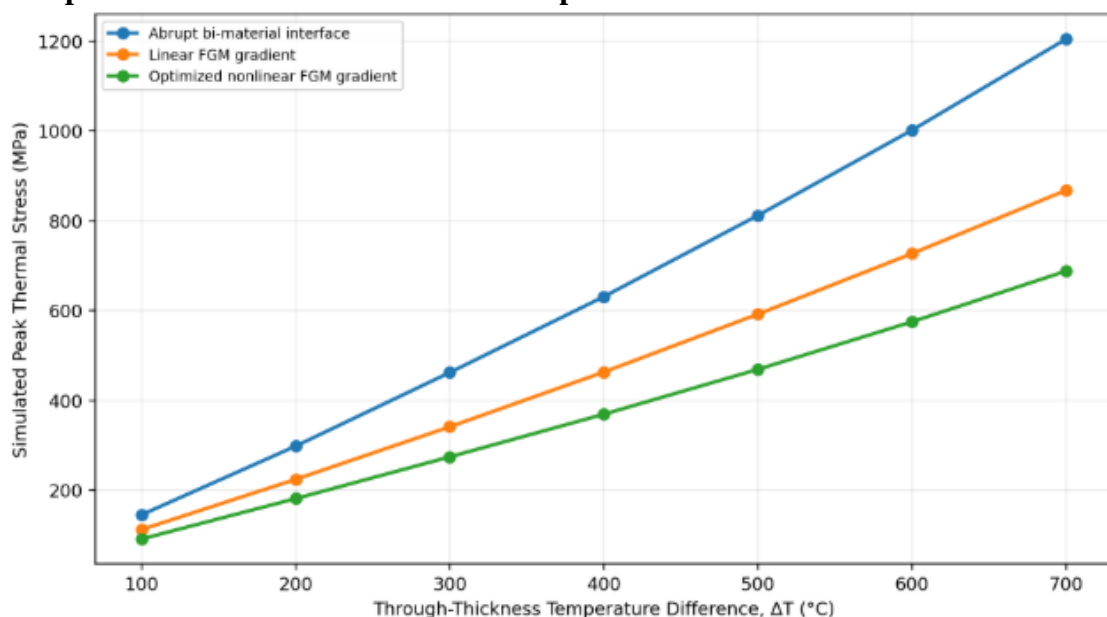
Table 2: Simulated Thermal Performance Under Representative Variable Environments

Material Architecture	VTEGI	Peak Stress at $\Delta T = 300$ °C	Peak Stress at $\Delta T = 500$ °C	Peak Stress at $\Delta T = 700$ °C	Principal Thermomechanical Characteristic
Abrupt bi-material interface	0.38	462 MPa	812 MPa	1,205 MPa	Strong localized expansion and stiffness mismatch
Linear functional gradient	0.69	341 MPa	592 MPa	868 MPa	Distributed mismatch but nonoptimized property profile
Optimized nonlinear gradient	0.87	274 MPa	469 MPa	688 MPa	Tailored stress redistribution and conductivity gradient

Note: The thermal stresses and VTEGI values are simulated and should not be interpreted as measured properties of a specific metal–ceramic system.

5.3 Response of Graded Architectures Across Variable Thermal Conditions

Graph 1: Simulated Thermal-Stress Response of Graded Material Architectures



The graph demonstrates a progressively widening difference among the three architectures as temperature difference increases. At mild thermal loading, all configurations remain comparatively close. As ΔT becomes more severe, the abrupt interface generates substantially greater peak stress than either graded architecture.

The nonlinear gradient consistently produces the lowest peak stress. This occurs because the compositional distribution is assumed to change more gradually in regions where thermal-expansion mismatch would otherwise produce severe stress and more rapidly in regions where stronger ceramic or metallic functionality is required.

The result is consistent with the theoretical premise of FGMs: thermal-stress resistance is improved when property discontinuity is replaced by a controlled spatial transition. Classical studies have long emphasized that the composition profile can be optimized to reduce thermal stress rather than merely graded arbitrarily.

Key Finding: Under variable thermal environments, the primary design advantage of an optimized FGM is not simply reduced average thermal stress but the suppression and spatial redistribution of the peak mismatch stress that would otherwise concentrate at an abrupt material interface.

6. Discussion

6.1 Gradient Shape Is a Thermomechanical Design Variable

The first implication of the study is that the gradient exponent or composition profile should be treated with the same engineering importance as constituent selection. Selecting a high-temperature ceramic and a ductile metal is only the beginning of FGM design.

The spatial transition determines how thermal conductivity, elastic modulus, thermal expansion, and therefore local stress evolve through thickness. Reddy's analytical treatment of graded plates demonstrated that material distribution influences thermomechanical stress and deformation directly. Noda similarly emphasized optimization of composition profiles specifically to reduce thermal stress and thermal-stress intensity around cracks.

This principle explains the simulated difference between linear and nonlinear gradients. A linear composition variation distributes the interface but does not necessarily distribute thermomechanical mismatch optimally. If one constituent's elastic modulus or thermal expansion changes sharply with composition, a linear material fraction may still create a nonlinear property discontinuity.

6.2 Variable Thermal Environments Require Temperature-Dependent Material Models

The second implication concerns material properties. Young's modulus, conductivity, coefficient of thermal expansion, specific heat, yield strength, creep resistance, and fracture behavior may all change significantly with temperature. Using room-temperature constants through a severe thermal gradient can therefore produce misleading predictions.

Variable thermal environments also require transient analysis. During rapid heating, the temperature gradient can temporarily become considerably greater than the eventual steady-state field. The component may consequently experience its most severe stress before reaching the maximum overall temperature.

Thermal shock further introduces fracture-mechanics considerations. Zhang and colleagues demonstrated that thermal-shock resistance of FGMs containing mixed-mode cracks depends upon local stress, thermal stress-intensity factors, and crack-propagation conditions. A design optimized only for uncracked elastic stress may therefore remain unsafe in a defect-tolerant engineering context.

6.3 Additive Manufacturing Enables Gradient Complexity but Adds New Constraints

The third implication is that advanced manufacturing enables far greater control over the gradient than was available when FGM theory was initially developed. Additive manufacturing can vary metallic feedstocks layer by layer or continuously during deposition and can potentially create three-dimensional composition fields rather than simple one-dimensional gradients. Reviews by Li and colleagues and Ghanavati and Naffakh-Moosavy describe this transition toward multi-scale, spatially programmable graded structures.

However, manufacturing freedom introduces processing physics that must be included in optimization. The intended composition profile may not be reproduced exactly because of melt-pool mixing, dilution, vaporization, powder-feed response time, solidification segregation, or deposition-path effects.

Material combinations may also form brittle intermetallic phases at intermediate compositions. A mathematically smooth gradient from Material A to Material B can therefore pass through a composition region that is metallurgically unstable.

7. Conclusion

Functionally graded materials provide a compelling architecture for engineering components exposed to variable thermal environments because they allow thermal, mechanical, and structural properties to change gradually within one component. Their principal advantage over conventional bi-material systems lies in replacing an abrupt property discontinuity with a spatially distributed transition. This is especially important when a heat-resistant ceramic must coexist with a tougher metallic structural region and the two constituents possess substantially different coefficients of thermal expansion and elastic response.

The methodological framework developed in this study combines thermal-expansion compatibility, conductivity control, modulus continuity, gradient smoothness, phase stability, and manufacturing fidelity within a Variable Thermal Environment Grading Index. The synthetic thermomechanical analysis demonstrates that material architecture substantially affects the magnitude of peak thermal stress. At a through-thickness temperature difference of 500 °C, the abrupt bi-material system produces a simulated peak stress of 812 MPa, the linear FGM produces 592 MPa, and the optimized nonlinear FGM produces 469 MPa. The approximately 42.2% modeled reduction relative to the abrupt interface illustrates the potential value of carefully tailoring the gradient.

The results also demonstrate why a functionally graded material should not be defined merely as any material containing a gradual composition change. The shape of the gradient is itself an engineering variable. Linear composition does not necessarily produce linear thermophysical properties, and the thermally optimal spatial distribution can change with temperature range, mechanical constraint, geometry, and transient heating conditions. Severe applications also require crack-sensitive thermal-

shock analysis, temperature-dependent constitutive properties, and consideration of residual stresses generated during fabrication.

Future empirical work should fabricate graded metal–ceramic or metal–metal specimens containing deliberately varied composition profiles and expose them to controlled steady, transient, and cyclic thermal conditions. Experimental validation should combine thermography or embedded temperature measurement, digital image correlation or high-temperature strain measurement, residual-stress analysis, microstructural and compositional mapping, thermal conductivity measurements, and fracture examination. Finite-element models should then be calibrated against the measured temperature and stress fields. Additive manufacturing provides a particularly important route for such research because it permits increasingly precise spatial control of material composition, but its metallurgical limitations must remain embedded within the optimization process.

References

1. Iqbal, M. D., Birk, C., Ooi, E. T., Pramod, A. L. N., Natarajan, S., Gravenkamp, H., & Song, C. (2022). Thermoelastic fracture analysis of functionally graded materials using the scaled boundary finite element method. *Engineering Fracture Mechanics*, 264, 108305. <https://doi.org/10.1016/j.engfracmech.2022.108305>
2. Zhang, Y., Guo, L., Wang, X., Shen, R., & Huang, K. (2019). Thermal shock resistance of functionally graded materials with mixed-mode cracks. *International Journal of Solids and Structures*, 164, 202–211. <https://doi.org/10.1016/j.ijsolstr.2019.01.012>
3. Peng, W., Chen, L., & He, T. (2021). Nonlocal thermoelastic analysis of a functionally graded material microbeam. *Applied Mathematics and Mechanics*, 42, 855–870. <https://doi.org/10.1007/s10483-021-2742-9>
4. Pandey, S., & Pradyumna, S. T. (2021). Thermal shock analysis of functionally graded sandwich curved beams using a new layerwise theory. *ZAMM – Journal of Applied Mathematics and Mechanics*, 101, e202100020. <https://doi.org/10.1002/zamm.202100020>
5. Wu, X., et al. (2021). Modeling and studies of fracture in functionally graded materials under thermal shock loading using peridynamics. *Theoretical and Applied Fracture Mechanics*, 111, 102852. <https://doi.org/10.1016/j.tafmec.2020.102852>
6. Yu, Q., Huang, Z., Zheng, G., Hu, W., Lei, C., Wang, Y., Jiao, Y., & Zhai, H. (2021). Thermal shock behavior of a novel $\text{TiC}_x\text{--Ni}_3(\text{Al,Ti})/\text{Ni}$ functionally graded composite. *Metals and Materials International*, 27, 5133–5144. <https://doi.org/10.1007/s12540-020-00836-0>
7. Li, H., et al. (2021). Thermal shock resistance and thermal insulation capability of laser-glazed functionally graded lanthanum magnesium hexaluminate/yttria-stabilised zirconia thermal barrier coating. *Materials*, 14(14), 3865. <https://doi.org/10.3390/ma14143865>
8. Sam, M., Jojith, R., & Radhika, N. (2021). Progression in manufacturing of functionally graded materials and impact of thermal treatment—A critical review. *Journal of Manufacturing Processes*, 68, 1339–1377. <https://doi.org/10.1016/j.jmapro.2021.06.062>
9. Boggarapu, V., Gujjala, R., Ojha, S., Acharya, S., Venkateswara Babu, P., Chowdary, S., & Gara, D. K. (2021). State of the art in functionally graded materials. *Composite Structures*, 262, 113596. <https://doi.org/10.1016/j.compstruct.2021.113596>

10. Jayachandiran, G., & Ramamoorthy, M. (2023). Advancements in manufacturing and vibration analysis of functionally graded polymer composites: A review. *Mechanics of Advanced Materials and Structures*. <https://doi.org/10.1080/15376494.2023.2289086>
11. *Recent trends and future outlooks in manufacturing methods and applications of FGM: A comprehensive review*. (2023). *Materials and Manufacturing Processes*, 38(9). <https://doi.org/10.1080/10426914.2022.2075892>
12. *The potential use of laser cladmed functionally graded materials to mitigate degradation in boiler tube heat exchangers for power plant applications: A review*. (2023). *Surface Engineering*, 39(6), 677–721. <https://doi.org/10.1080/02670844.2023.2249653>
13. Jin, Z. H., & Batra, R. C. (2012). Thermal shock resistance of functionally graded materials. In *Encyclopedia of Thermal Stresses*. Springer. https://doi.org/10.1007/978-94-007-2739-7_87
14. Reddy, J. N. (2000). Analysis of functionally graded plates. *International Journal for Numerical Methods in Engineering*, 47, 663–684.
15. Sankar, B. V. (2001). An elasticity solution for functionally graded beams. *Composites Science and Technology*, 61(5), 689–696.
16. Praveen, G. N., & Reddy, J. N. (1998). Nonlinear transient thermoelastic analysis of functionally graded ceramic-metal plates. *International Journal of Solids and Structures*, 35(33), 4457–4476.
17. Tanigawa, Y. (1995). Some basic thermoelastic problems for nonhomogeneous structural materials. *Applied Mechanics Reviews*, 48(6), 287–300.
18. Miyamoto, Y., Kaysser, W. A., Rabin, B. H., Kawasaki, A., & Ford, R. G. (1999). *Functionally Graded Materials: Design, Processing and Applications*. Springer.
19. Birman, V., & Byrd, L. W. (2007). Modeling and analysis of functionally graded materials and structures. *Applied Mechanics Reviews*, 60(5), 195–216.
20. Udupa, G., Rao, S. S., & Gangadharan, K. V. (2014). Functionally graded composite materials: An overview. *Procedia Materials Science*, 5, 1291–1299.