Chapter 1

Advances in Functionally Graded Ceramics – Processing, Sintering Properties and Applications

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Additional information is available at the end of the chapter

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Abstract

In multilayered structures, sharp interface is formed between the layers of dissimilar materials. At this interface, the large difference in thermal expansion coefficients of the two dissimilar materials generates residual thermal stresses during subsequent cooling. These stresses lead to cracking at the interface, and these cracks lead to the deterioration of mechanical properties, and finally crack propagation leads to the delamination of the multilayered structure. Scientific progress in the field of material technology, and the continuing developments of modern industries have given rise to the continual demand for ever more advanced materials with the necessary properties and qualities. The need for advanced materials with specific properties has brought about the gradual transformation of materials from their basic states (monolithic) to composites. Recent advances in engineering and the processing of materials have led to a new class of graded multilayered materials called Functionally Graded Materials (FGMs). These materials represent a second generation of composites and have been designed to achieve superior levels of performance. This chapter looks at the best processing technologies and the uses and applications of the advanced, high quality products generated, and also presents an extensive review of the recent novel advances in Functionally Graded Ceramics (FGCs), their processing, properties and applications. The manufacturing techniques involved in this work have involved many concepts from the gradation, consolidation and different sintering processes. Each technique, however, has its own characteristics and disadvantages. In addition, the FGC concept can be applied to almost all material fields. This chapter covers all the existing and potential application fields of FGCs, such as engineering applications in cutting tools, machine parts, and engine components, and discusses properties of FGCs such as heat, wear, and corrosion resistance plus toughness, and their machinability into aerospace and energy applications.

Keywords: Functionally graded ceramics (FGCs), Classification, Design and processing, Applications

1. Introduction

The result of scientific progresses in materials science and the continuing developments of modern industry, have given rise to the continual demand for advanced materials that can satisfy the necessary advanced properties and qualities. This requirement for advanced materials with specific properties brought about the gradual transformation of materials from their basic states(monolithic) to composites. Recent advances in engineering and the processing of materials have led to a new class of materials called Functionally Graded Materials (FGMs). These represent a second generation of composite materials and have been designed to achieve superior levels of performance.

FGMs are a type of composite material and are classified by their graded structure. Specifically, an FGM typically consists of a composite material with a spatially varying property and is designed to optimize performance through the distribution of that property. It could be a gradual change in chemical properties, structure, grain size, texturization level, density and other physical properties from layer to layer. FGMs have a graded interface rather than a sharp interface between the two dissimilar materials. Using a material with, for example, a graded chemical composition, minimizes the differences in that property from one material to another. No obvious change may take place in their chemical composition if the gradient is smooth enough, and if the transition is smooth, the mismatches in the property from one point in the material to another will be limited. Therefore, the ideal FGM has no sharp interfaces. Moreover, there will be no single location that is inherently weaker than the rest of the composite.

The aim of the production of FGMs is the elimination of the macroscopic boundary in materials in which the material's mechanical, physical and chemical properties change continuously and have no discontinuities within the material. Thus, these materials exhibit superior mechanical properties when compared to basic (monolithic) and composite materials.

In the past, the composition of FGMs typically included at least one metal phase. Recently, great attention has been devoted to ceramic-ceramic and glass-ceramic systems due to their attractive properties. Ceramic materials are designed to withstand a variety of severe in-service conditions, including high temperatures, corrosive liquids and gases, abrasion, and mechanical and thermal induced stresses. In this chapter, special attention will be given to the new advances in Functionally Graded Ceramics (FGCs), their processing and applications.

2. Origin of FG ceramics concept

The FGCs concept originated in Japan in 1984 during the space plane project of Niino and coworkers [1] in the form of a proposed thermal barrier material capable of withstanding a surface temperature of 2000K and a temperature gradient of 1000K in a cross-section of <10 mm. It is difficult to find a single material able to withstand such severe conditions. The researchers used the FGM concept to manufacture the body of a space plane using material with high refractoriness and mechanical properties resulting from gradually changing

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compositions. They designed a ceramic material for the outer surface that is exposed to a high temperature environment and a thermally conductive metal for the inner surface. In 1987, the successful FGC research was accepted for use in a major project by the Ministry of Education and Science. During the period 1987–1991, a research project entitled "*Research on the generic technology of FGM development for thermal stress relaxation*" was conducted by Japanese scientists. In 1992, FGMs were selected as one of 10 most advanced technologies in Japan. Since then, FGM technology has grown in importance and has garnered the attention of many authors throughout the world. Although FGMs were invented fairly recently, these materials are not actually new. Gradual variations in the microstructure of materials have been explored for millions of years by the living organisms. FGMs have been long established in nature (bio-tissues of plants, bamboos, shells, coconut leaves and animals) and are even found in our bodies — such as in bones and teeth. [2].

3. Classification of FG ceramics

Future applications will demand materials that have extraordinary mechanical, electronic and thermal properties which can tolerate different conditions and yet are easily available at a reasonable price. As a result, it becomes necessary to reinforce at least one ceramic material in the functionally graded structure. FGM-based ceramic reinforcement is able to withstand high temperature environments due to the higher thermal resistance of the ceramic constituents and their attractive properties. Functionally graded ceramic compositions can be classified into:

3.1. Ceramic/metal

Due to the appearance of new industries that require high temperature and aggressive media, it became important to insert at least one ceramic material phase in any advanced FGM due to its attractive properties. In this type of FGC, the desirable properties of both metals and ceramics are combined. For example, we can use the high thermal conductivity and toughness of metals as an internal surface and combine it with the greater hardness and thermal insulation of ceramics as an external surface, thereby enabling the material to withstand high temperature environments. Examples of this type are the **(Ti-TiB_2) FGC** that is used as an armor material [3] and (Ni/Al_2O_3) **FGCs** which are used as lightweight armor materials with high ballistic efficiency [4].

In addition, ceramic/metal FGCs can be designed to reduce thermal stresses and to take advantage of both the heat and corrosion resistances of ceramics, and the mechanical strength, toughness, good machinability and bonding capability of metals — without severe internal thermal stresses.

3.2. Ceramic/ ceramic and glass/ ceramic

By exploiting the myriad possibilities inherent in the ceramic/ceramic FGCs concept, it is anticipated that the properties of materials will be optimized and new uses for them will be discovered. Examples of these FGCs are **alumina/zirconia**, a material used in biomedical and structural applications, **mullite/alumina,** which is used as a protective coating for **SiC** components in corrosive environments [2, 5]. **Zirconia-mullite/alumina** FGCs can be used as refractory materials in high temperature applications, as well as being suitable for engineering and tribological applications [6, 7].

3.3. Ceramic/ polymer

An example of this type of FGC is the **boron carbide/polymer** FGC. Due to its light weight and flexibility, the BC/polymer FGC is used in lightweight armor and wears related applications [8]. The feature of this FGC is that the ceramic with graded porosity is fully dense on the front surface changing to open porosity on the back surface. The polymer is then infiltrated into the porous side of the ceramic plate to provide a lightweight energy-absorbing backing. A ballistic fiber weave, such as Kevlar, could also be embedded in the polymer to provide constraint and enhanced ballistic protection.

Ceramic/ polymer FGCs could also find applications in reducing the wear of automotive components. Additionally, they are used in many industrial applications requiring materials that are resistant to wear, corrosion, and erosion in hostile environments. Also, this type of FGC can be used in nuclear applications, such as the manufacture, handling and storage of plutonium materials [8].

Recently, the introduction of porosity in ceramic/polymer FGCs has broadened the scope of their application in the fields of biomedicine and tissue engineering [9, 10]. Due to the large surface area, high porosity, low thermal conductivity and high-temperature resistance of the porous ceramics, they were widely used in many fields, such as functioning as supports for ceramic filters, as artificial bones, high temperature insulators, and active cooling parts.

4. Design and processing of FG ceramics

The processing of advanced ceramics is a complex operation requiring several process control steps to achieve the ultimate product performance in the end. A successful forming technique leads to a ceramic product with an engineered microstructure which is characterized by a small defect size and by a well-distributed homogeneous grain boundary composition in order to achieve optimal performance and a high degree of reliability.

The manufacture of FGCs can be divided into two steps, namely gradation and consolidation. Gradation is the building of the spatially inhomogeneous graded structure, while consolidation is the transformation of this graded structure into the bulk material. The gradation process is usually classified into three main groups: constitutive, homogenizing, and segregating processes. The stepwise creation of a graded material from precursor materials is the basic constitutive process. In the homogenizing processes, the sharp interface between the two materials is converted to a gradient by material transport i.e. diffusion. In the segregating process, the macroscopically homogeneous material is converted into a graded material by an external gravitational or electric field. The primary advantage of the homogenizing and segregating processes is the production of a continuous gradient. Following this, drying and sintering (or solidification) steps need to be adapted relevant to the particular material selected, and attention has to be paid to the different shrinkage rates during the sintering of FGCs [11].

The manufacturing process is one of the most important areas of FGC research. A large part of the research into FGCs has been dedicated to processing, and a large variety of production methods have been developed for use in the processing of FGCs. Most of the processes of FGC production are based on variations of conventional processing methods, which are already well-established. Methods that are capable of accommodating a gradation step include powder metallurgy [12-14], sheet lamination, chemical vapor deposition and coating processes. In general, the forming methods used include centrifugal casting [15-17], slip casting, tape casting [18], and thermal spraying [19, 20]. Which of these production methods is the most suitable? It depends mainly on the material combination, the type of transition function required, and the geometry of the desired component. However, it was found that powder metallurgy (PM) will be the most suitable method for the manufacture of FGCs in the future. It is believed that the main issue in the implementation of the PM method is the sintering process, which needs to be explored further in order to achieve improvements in the microstructure and mechanical properties of the resulting FGCs [21].

4.1. Powder metallurgy

Powder metallurgy (PM) is one of the most prevalent techniques due to its wide range control of composition, its microstructure and its ability to form a near net shape. It is a cost-effective technique and has the advantages of greater availability of raw materials, simpler processing equipment, lower energy consumption and shorter processing times. In powder processing, the gradient is generally produced by mixing different powders in variable ratios and stacking the powder mixtures in separate layers.

The thickness of the separate layers is typically between 0.2 mm and 1mm. Several techniques have been introduced for powder preparation, such as chemical reactions, electrolytic deposition, grinding or comminution. These techniques permit the mass production of powder form materials and usually offer a controllable size range of the final grain population. In powder processing, the main consideration focuses on the precision in weighing of amounts of individual powders and the dispersion of the mixed powders. These elements will influence the properties of the structure and need to be handled very carefully. In the subsequent processes, the forming operations are performed at room temperature, while sintering is conducted at atmospheric pressure as the elevated temperature used may cause further reactions that may affect the materials [22]. [23] studied the manufacturing method of another constituent, **ZrO_2/AISI316L FGCs** for use in joint prostheses. The mechanical and biotribological properties of the FGCs were evaluated through studies of their fracture toughness, bending strength, and wear resistance. It was found that FGMs with a layer thickness of less than 1.0 mm showed a low wear resistance. FGCs with a layer thickness of more than 2 mm, therefore, have mechanical and biotribological properties which are suitable for use in joint prostheses. [24] studied the relative density, linear shrinkage and Vickers hardness of each layer of **8YSZ/Ni FGC**. The microstructure and the composition of these components were also studied. The results obtained showed that FGCs produced by spark plasma sintering exhibited a low porosity level and consequently fully dense specimens. There are no macroscopic distinct interfaces in **YSZ/Ni** FGM due to the gradual change in components. Another successful FGC prepared by the PM method is **ZrO_2/NiCr** FGC, as studied by [12].

4.2. Hot pressing

Yittria stabilized zirconia **(YSZ)** and nickel 20 chromium **(NiCr)** are the two materials combined using **YSZ-NiCr FGC** interlayer via the hot pressing method [25]. At the initial stage of processing, the powdered YSZ and NiCr were mixed in a ball milling machine for 12 hours before being stacked layer-by-layer in a graphite die coated with boron nitride. In this study, the concept of stepwise gradation was applied by arranging the composition of each layer to be a certain desired percentage. The preoccupation of each layer was performed at a lower pressure before stacking the adjacent layer under higher pressure (10 MPa) to ensure an exact compositional distribution within the layers.

A new composition profile of 15 layers with a crack-free joint of the **Si_3N_4-Al_2O_3 FGC** was proposed using the hot pressing technique [26]. Bulk SiC/C FGC is another pair successfully manufactured using the hot pressing process. In terms of thermal properties, the hot pressed SiC/C FGC was found to have a high effective thermal conductivity at the interface of the 1 mm SiC layer when compared to the specimens prepared using other methods. No cracks were found in the SiC/C coatings, as a result of the high thermal fatigue behavior of the FGC. The plasma-relevant performance also indicated that the specimen has excellent high temperature erosion resistance [27]. Moreover, hot pressed **hydroxyapatite/Ti (HA/Ti) FGC** showed a strong biocompatibility and a high bonding strength with the bone tissue of rabbits, as investigated by [28]. The study concluded that the HA/Ti FGC has a good potential for use in hard tissue replacement applications as it possesses a high bonding strength which could exceed the 4.73 MPs shear strength of new bone tissues when compared to pure Ti metal. Amongst the successfully manufactured hot pressed FGCs are the novel **TiB_2/ZrO_2** and **TiB_2-SiC/ZrO_2 FGCs** which show excellent properties and have been identified for possible use in ultra-high temperature applications [29].

4.3. Cold pressing

A beam-shaped porous lead zirconia titanate-alumina **(PZT-Al_2O_3) FGC** actuator that exhibits the theoretically matched electric-mechanical response with a crack-free structure based on the pyrolyzable pore-forming agent (PFA) porosity gradient, has been successfully manufactured using a cold sintering method [25].

The binder addition is similarly applied in the manufacture of another FGC composed of Ni and **Al_2O_3** in order to investigate the influence of the particle size used. In this study, the appropriate Ni, Al_2O_3 and Q-PAC 40 (organic binder) particle sizes were selected, based on the desired microstructure of the corresponding composition. After being mixed together in the blending process, the powder mixtures were cold pressed under 86 MPa pressure. This was followed by pressureless sintering at 1350°C with specific sintering [30]. The titanium/hydroxyapatite **(HA/Ti)** and other FGC implants with a gradually changing composition in the longitudinal direction of the cylindrical shape were also manufactured via cold isostatic pressing (800 to 1000 MPa) in order to optimize the mechanical and biocompatibility properties of the resultant structures [31]. Figure 1 shows the flow chart outlining the manufacturing process of the cold pressed Al_2O_3-ZrO_2 FGC used in the study [30]. Different elemental consideration under powder characteristic in terms of the addition of the space holder material was investigated on porous Ti-Mg (titanium-magnesium) FGM.

Most researchers working with this technique increasingly intend to use microscale particles in the manufacture of FGCs since nanoparticles need greater precision during processing. Only a small number of limited studies report using nano-sized composition particles [21]. **Co/α-Al_2O_3 FGC** composed of nano-sized powders was successfully manufactured using a high pressure torsion procedure [32]. This procedure is classified as a PM method, and cold pressing — as the consolidation or sintering process — is performed after compaction. The difference is only in the way of delivering the pressure in the torsional mode.

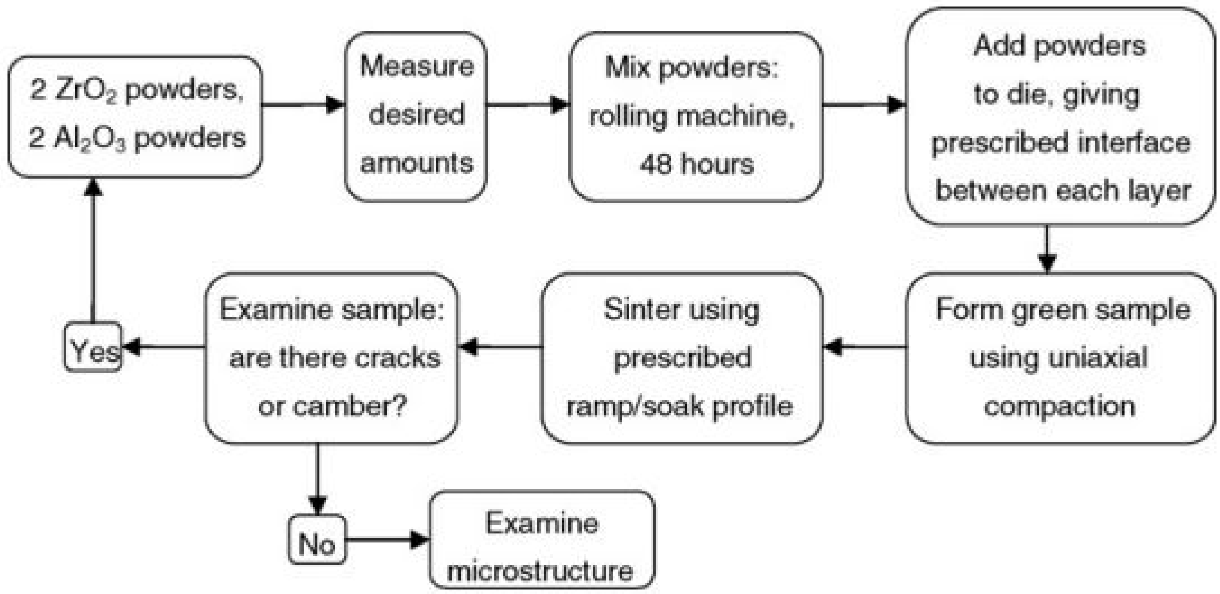

Figure 1. Flow chart detailing the manufacturing process of Al_2O_3/ZrO_2 FGC [30].

4.4. Sintering process

The sintering process is performed simultaneously with the compaction process if the FGC is prepared using a hot pressing process. However, in the cold pressing process, the sintering process is performed only after the powders have been compacted. The effectiveness of three different sintering methods, including electric furnace heating, high frequency induction heating, and spark plasma sintering (SPS) were investigated, [33]. SPS is a newly developed process which enables the sintering of high quality materials in short periods by charging the intervals between powder particles with electrical energy. Their systems offer many benefits in terms of ease of operation, low cost, a more uniform and rapid sintering compared to the conventional systems using hot press sintering, hot isostatic pressing or atmospheric furnace processes applied to many advanced materials. Amongst the reported SPS FGCs are WC based materials **(WC/Co, WC/Co/steel, WC/Mo),** and **ZrO_2** based composites **(ZrO_2/steel, ZrO_2/TiAl, ZrO_2/Ni), Al_2O_3/TiAl**, etc. [34]. The influence of **ZrO_2** content and sintering temperature on microstructures and mechanical properties of the composites were investigated by [35].

In order to evaluate the sintering performances, one of the parameters that could be investigated is the porosity. As a result, some sintering models have been developed and analyzed to this end. These studies proved that the amount of porosity is directly related to the rate at which shrinkage occurs [36]. The changes in porosity and shrinkage in the theoretically sintered nickel/alumina **(Ni/Al_2O_3) FGC** have been studied [37]. This study shows how the porosity reduction model can be used to access the quality of particle-reinforced metal-ceramic FGCs formed by pressureless sintering and to predict the changes that can be achieved in porosity reduction through the engineering of the particle dispersion in the processing of FGCs. The influence of other sintering parameters including time, temperature, sintering atmosphere and the isostatic condensation on the performance of the resulting FGCs, was investigated [38]. During the manufacture of the sintered tool gradient materials — composed of **wolfram carbide** and cobalt — used in the study, the sintering parameters were changed in order to find their optimum values. The sequential concentration of the molding, with layers having an increasing content of carbides and a decreasing concentration of cobalt and sintering, ensures the acquisition of the required properties, including resistance to cracking. Another successful example of pressureless sintering is the functionally graded zirconia-mullite/alumina ceramics **(ZM/A FGC).** These exhibit a homogenous structure with highly improved and unique properties. The recorded value of each test of tailored FGZM/A was nearly equal to the average of the test values of its non-layered composites. This is good evidence of the strength of the interfacial bonding between subsequent layers of the composite as well as the homogeneity and uniformity of the powders in each layer [6, 7].

4.5. Infiltration process

Infiltration, or to give it the correct scientific terminology — hydrology —is the process by which fluid on the ground surface precipitates into the soil. This process is governed by the force of either gravity or capillary action. The rate of infiltration depends on soil characteristics such as storage capacity, transmission rate through the soil, and the ease of entry of the fluid.

The infiltration method was introduced in order to prepare certain complex FGCs shape. This manufacturing method needs little or no bulk shrinkage and more rapid reaction kinetics. As the common process for mold shaping is the heating of the powder to a temperature that is higher than the liquid phase, the demand of ensuring there is no bulk shrinkage is quite challenging.

A compositionally graded **Al-SiC FGC** was successfully manufactured using the pressureless infiltration method in the early part of the last decade. This indicated that the thermal conductivity of the FGC produced increased in a nonlinear manner, while the volume fraction of the ceramic element decreased [39]. An innovative method of infiltration processing using microwave sintering and an environmental barrier coating (EBC) was subsequently developed for the manufacture of **Si_3N_4 FGC**. This FGC is composed of **α-Si_3N_4-Yb-silicate** green parts and porous **β-Si_3N_4** ceramics as the substrates [40]. Figure 2 shows the successful manufacture of **YSZ/SiC FGC** via the infiltration method, as investigated by [41]. In addition, different compositions of porous **Ti/HAP FGCs** were also manufactured using the infiltration technique. The Young's Modulus of the manufactured FGCs was comparable to human cortical bone in the porosity range of 24 to 34%, [42]. The effect of glass infiltration was investigated on the **CaO-ZrO_2-SiO_2 system** in the development of **glass/alumina FGCs.** In order to obtain the final compositional gradient which is indicated by blue glass, the glass formulation of the system was doped with cobalt by adding a small molar percentage (0.1 mol %) of CoO. Characterization of the specimens proved that the cobalt-doped glass has interesting mechanical properties, including a high elastic modulus, good fracture toughness, and an acceptable coefficient of thermal expansion [43].

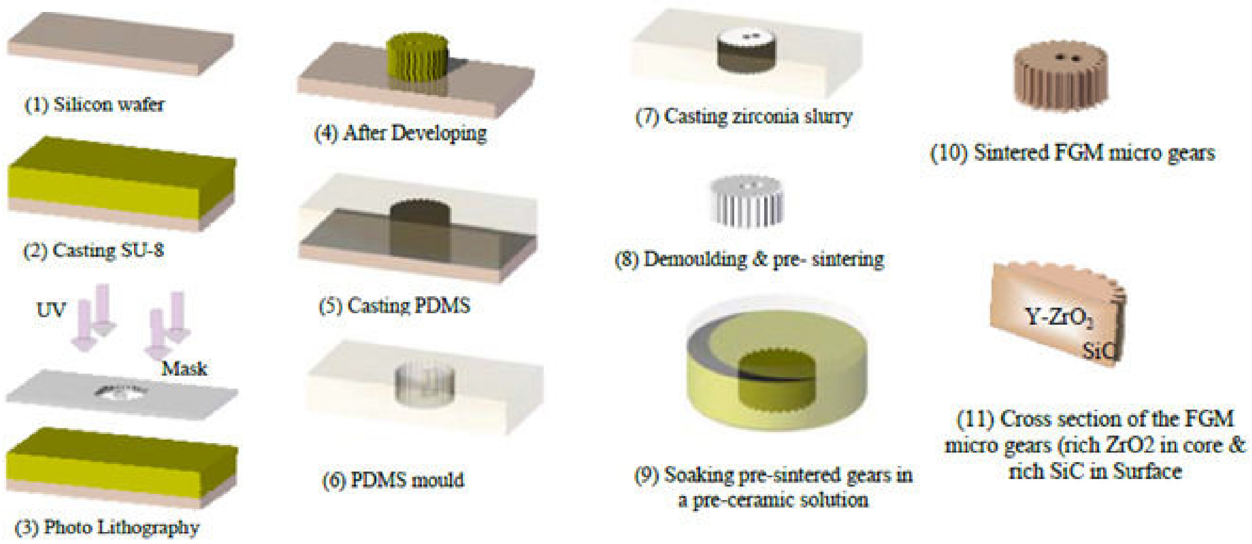

Figure 2. Schematic diagram of the infiltration process of YSZ/SiC FGM [41].

4.6. Centrifugal casting

Centrifugal casting is one of the most effective methods used in the processing of FGCs due to its wide range control on composition and microstructure. The microstructure and composition gradients in some aluminum based FGCs including **Al/SiC, Al/Shirasu, Al/Al_3Ti, Al/Al_3Ni,** and **Al/Al_2Cu** combinations have been made by evaluating the dispersion of the different phase particles within the FCM structures manufactured via different centrifugal casting processes [44]. The study found that **Al/SiC, Al/Shirasu** and **Al/Al_3Ti FGCs** can be manufactured using the centrifugal solid-particle method, while the centrifugal in-situ method is suitable for the manufacture of Al/Al_3Ni and Al/Al_2Cu FGMs. The combination of both processing methods is required for **Al/(Al_3Ti+Al_3Ni)** hybrid FGCs.

The phase compositions of FGCs manufactured using this approach depend strongly on the condition of the centrifugal sedimentation process. Relevant factors include the duration of the process, rotation speed, and solid and dispersive fluid contents [45]. A self-propagating high temperature synthesis reaction is added as one of the steps, followed by centrifugal casting, in the manufacture of TiC-reinforced iron base **(Fe-TiC) FCC**. Observation of the manufactured specimen indicated an increasing trend in the hardness profile from the outer surface to the TiC-rich inner surface. The wear performance of the TiC-rich inner face was found to be better when compared to the particle free outer surface of ferritic steel matrices [46].

The formation of gradient solidification is another aspect that was evaluated in the investigation into FGCs manufactured via centrifugation. In this study, **SiC, B_4C, SiC- graphite** hybrid, primary silicon, **Mg_2Si** and **Al_3Ni** reinforced aluminum based FGCs were prepared using centrifugal casting. The densities and the size of the reinforcements were found to be two major factors influencing the formation of the graded microstructure [47].

4.7. Slip casting

TZP/SUS304 FGC was developed using a slip casting technique [48]. The gradual distribution of the chemical composition and microstructure of the manufactured specimens eliminated the macroscopic FGC interface that occurs in a traditional ceramic/metal joint. Another FGC material that was successfully manufactured via the slip casting method is **Al_2O_3/W FGC**, which has the potential to be used as a conducting and sealing component in high-intensity discharge lamps (HiDLs) [49].

4.8. Thermal spraying

Thermal spraying has been frequently used to produce FGC coatings. Thermal spraying of FGCs offers the possibility of combining highly refractory phases with low-melting metals, and allows for the direct setting of the gradation profile. [50] studied the heat insulation performance of thermal barrier-type FGC coatings under a high heat flux. The FGC coatings with thicknesses varying from 0.75 to 2.1 mm were designed and deposited onto a steel substrate using plasma spraying. [51] studied and investigated the different properties, microstructure and chemical composition of FG 20 wt.% **MgO-ZrO_2/ NiCrAl** thermal barrier coatings that were obtained using the plasma spraying process. Scanning Electron Microscope (SEM) observations of the fractured surface revealed that the intermediate graded layer had the compositional mechanical properties of strength and toughness, due to improvement of the microstructure and relaxation of the residual stress concentration. In another study, the spark plasma technique used in the thermal spraying process was employed in the manufacture of an FGC composed of Hydroxyapatite **(HAp)** and titanium nitride **(TiN)** [52]. In order to improve the adhesion between the adjacent graded layers of the FGC, a proper bond coat should be introduced. It is thought that by arranging the smooth change of the mismatch between the thermal expansion coefficients of the composition, the delamination within the FGC structure could be addressed. Other FGCs manufactured using this technique are **HAp/TiO_2, Yttria stabilized zirconia (YSZ)/mullite** coats deposited on **SiC** substrates [53] and tungsten carbide/cobalt **(WC/Co) FGC** [54].

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4.9. Laser cladding

In the laser cladding process, two or more dissimilar materials are bonded together using laser intercession. During the process, the material which is in powdered form is injected into the system — which is purpose-built for the cladding process — while the laser, which causes melting to occur, is deposited onto the substrate. Although the technique has become the best method for coating various shapes and has been declared to be the most suitable process for applications with graded material, limitations still exist because the setup of the high technology system processes is very expensive and is unsuitable for mass production as a result of the layer-by-layer process. The Nd:YAG type of laser was also being used in the manufacture via selective laser melting (SLM) of super **nickel alloy and zirconia FGC**, Figure 3. The resulting materials contained an average porosity of 0.34% with a gradual change between the layers, and without any major interface defects [55]. The final **WC-NiSiB alloy FGC** product manufactured by this method was found to be suitable for use in high-temperature tribological applications. The study mentioned that the surface roughness and the geometrical properties of the synthesized FGCs can be controlled by adjusting the heat input during the laser cladding process [56].

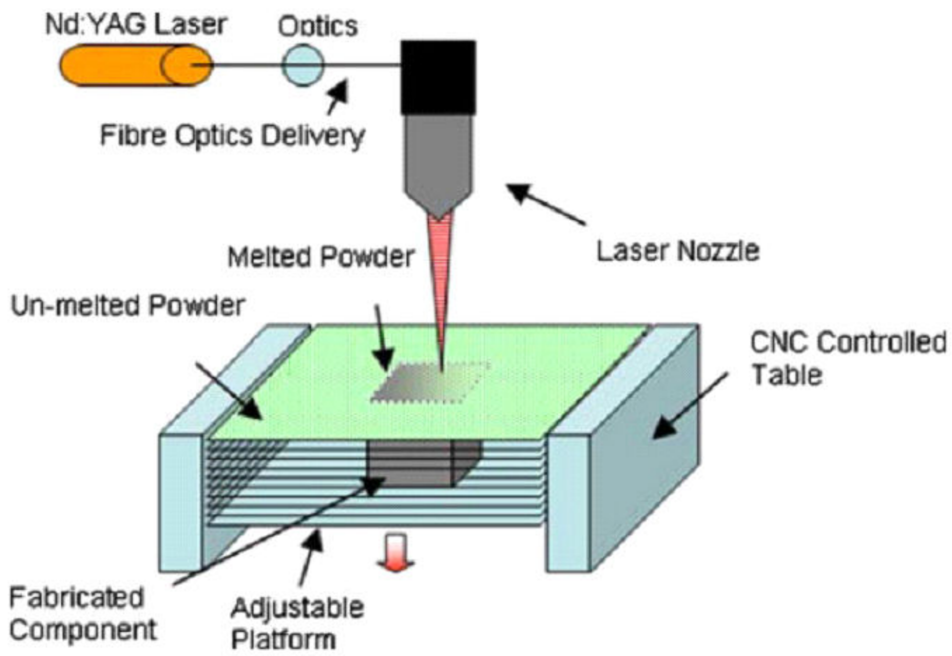

Figure 3. Experimental setup used for laser assisted processing using an Nd:YAG laser power source [55].

4.10. Vapor deposition method

Vapor deposition is a process by which materials in the vapor phase are condensed to form a solid material. This process is generally employed to make coatings for the alteration of the properties of the substrates such as mechanical, electrical, thermal, and wear etc. Basically, vapor deposition is classified into two categories, namely chemical vapor deposition (CVD) and physical vapor deposition (PVD). C-based materials that have an excessive chemical sputtering which yields at 600 to 1000 K and exhibits irradiation with enhanced sublimation at >1200 K when exposed to plasma erosion conditions, were successfully manufactured via the CVD method in 2002. The problem of serious C-contamination of the plasma was solved by using chemically deposited SiC coatings on the surface of the C-substrate. C-based FGCs such as **SiC/C, B_4C/Cu, SiC/Cu and B_4C/C bulk FGC** were also successfully manufactured using this method [57].

5. Advanced applications of FGC ceramics

The use of FGCs has rapidly gained popularity in recent years, especially in high temperature environments and aggressive media, as illustrated in Figure 4. The FGCs concept is applicable to almost all material fields. Examples of a variety of real and potential applications of FGCs in the field of engineering are cutting tools, machine parts, and engine components, while incompatible properties such as heat, wear, and corrosion resistance, plus toughness and machinability are incorporated into a single part. For example, throwaway chips for cutting tools made of graded tungsten carbide/cobalt **(WC/Co)** and titanium carbonitride **(TiCN)-WC/Co** that incorporate the desirable properties of high machining speed, high feed rates, and a long life have been developed and commercialized. Various combinations of these ordinarily incompatible functions can be applied to create new materials for the aerospace industry, chemical plants, optoelectronic applications, bio-medical applications, solar cells, and nuclear energy reactors.

5.1. FG Ceramics for aerospace, military and automotive applications

Thermal barrier coating FGCs are used for military and commercial aero engines as well as in gas turbine engines for automobiles, helicopters, marine vehicles, and electric power generators. They are also used in augmentor components, e.g. tail cones, flame holders, heat shields and duct liners, and in the nozzle section they are being used experimentally in the verging/diverging flaps and on seals where hot gases exit the engine [58, 59].

Space vehicles flying at hypersonic speeds experience extremely high temperatures from aerodynamic heating due to friction between the vehicle surface and the atmosphere. One of the main objectives of investigating FGCs deposited by chemical vapor deposition (CVD-FGCs) was the development of thermal barrier coatings (TBCs) for a space plane. It was found that sheets of **SiC/C FGCs** produced by CVD provide excellent thermal stability and thermal insulation at 1227°C, as well as excellent thermal fatigue properties and resistance to thermal shock [60]. A combustion chamber with a protective layer of SiC/C FGC has been developed for the reaction control system engine of HOPE, a Japanese space shuttle. These FGCs produced for rocket combustors have undergone critical tests with nitrogen tetroxide and monomethyl hydrazine propellants at firing cycles of 55 seconds with subsequent quenching by liquid nitrogen. The maximum outer wall temperature of these model combustors was 1376°C to 1527°C, while the inner wall temperature reached 1677°C to 2027°C. No damage to the

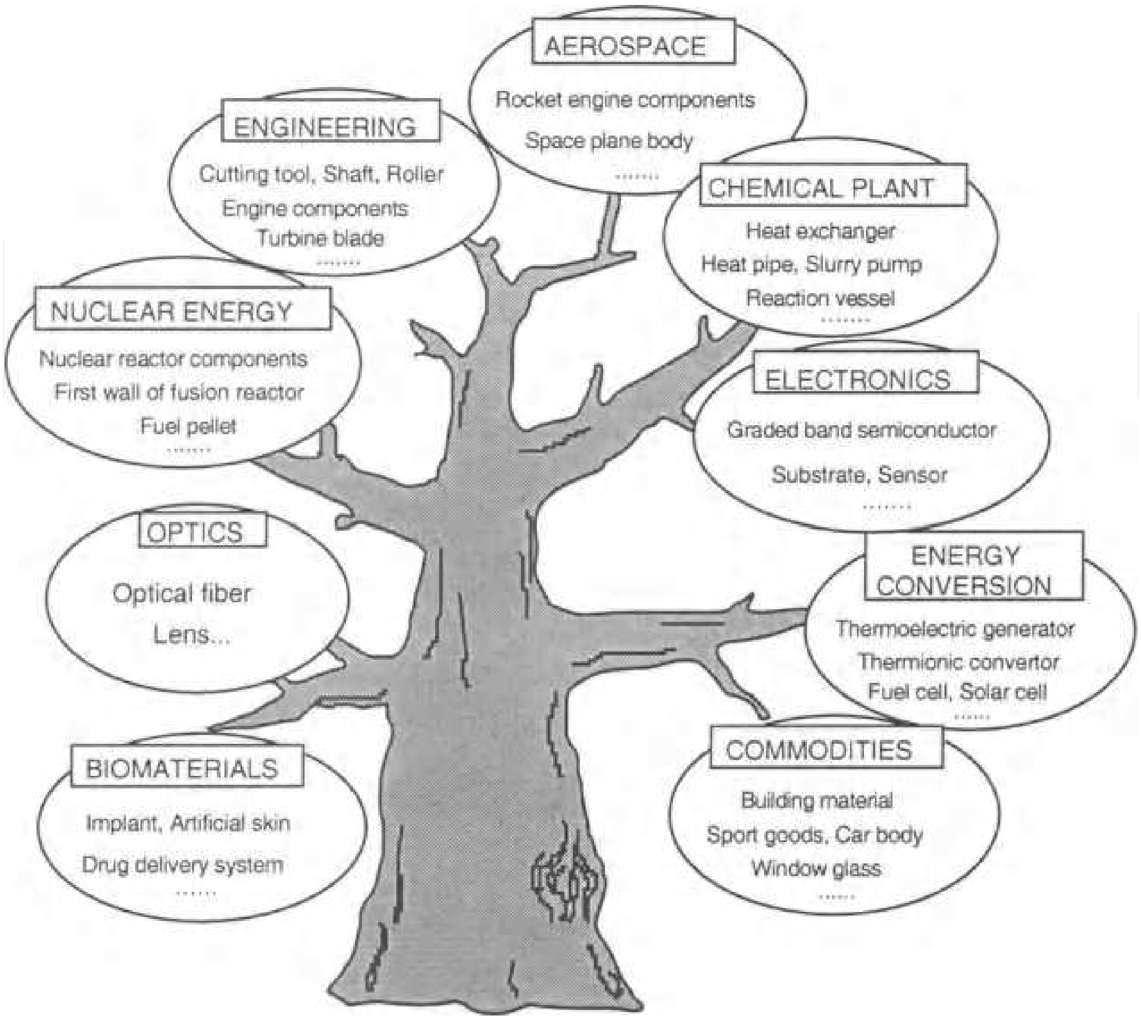

Figure 4. Areas of potential application of FGCs.

combustors was observed after two test cycles [61]. It is expected that the Si-based ceramics, **SiC** and **Si_3N_4**, will be introduced in the hot-sections of the next generation of gas turbines operating at higher temperature. **Mullite/SiC** TBC FGC exhibited excellent adhesion and corrosion resistance as shown in the study by [62].

Graded zirconia/nickel **ZrO_2/Ni** and **Al_2O_3/ZrO_2 FGC** TBCs have also been considered for other rocket engines, such as in the small regeneratively cooled thrust chambers in orbital maneuvering systems [63, 64]. These chambers are prepared using a combination of galvano-forming and plasma spraying. No delamination of ZrO_2 was observed after 550 seconds of combustion.

Nowadays it is necessary to reduce the weight of army systems in order to cope with the rapidly developing requirements of military contingencies. Ultralight weapons will be the cornerstone of future battlefield domination. Military strategists have asked for radical weight reductions in future military equipment, which will need new materials in new structures and designs. The concept of FGCs is one of the material technologies identified for this purpose [65].

Stealth missiles are now a required component of a modern weapons system. Parts made from specific materials can be used to absorb the electromagnetic energy emitted in order to minimize waves reflected in the direction of the enemy radar receiver. The most promising new materials for use in these applications are ceramic matrix composites reinforced with ceramic woven fabrics. The use of long, continuous ceramic fibers embedded in a refractory ceramic matrix creates a composite material with much greater toughness than basic (monolithic) ceramics, and which has an intrinsic inability to tolerate mechanical damage without brittle fracture. **Nicalon SiC fibers**, which have semiconducting properties, and **Nextel mullite ($3Al_2O_3$- $2SiO_2$- 0.1 B_2O_3) fibers**, which are completely dielectric, are used in the preparation of graded oxide matrix ceramic composites [66].

Some structural ceramics such as **B_4C, SiC, Al_2O_3**, AlN, TiB_2 and Syndie (synthetic diamond) FGCs [67–70] are viewed as potential materials for use in armor applications for both personnel and vehicle protection, owing to their low density, reliability, superior hardness, compressive strength and greater energy absorption capacity, which enable effective protection from projectiles.

Moreover, spark plasma sintered **Ti/TiB_2, TiB_2 /$MoSi_2$** [71] and Ni/Al_2O_3 [4], FGCs are used as lightweight armor materials with high ballistic efficiency.

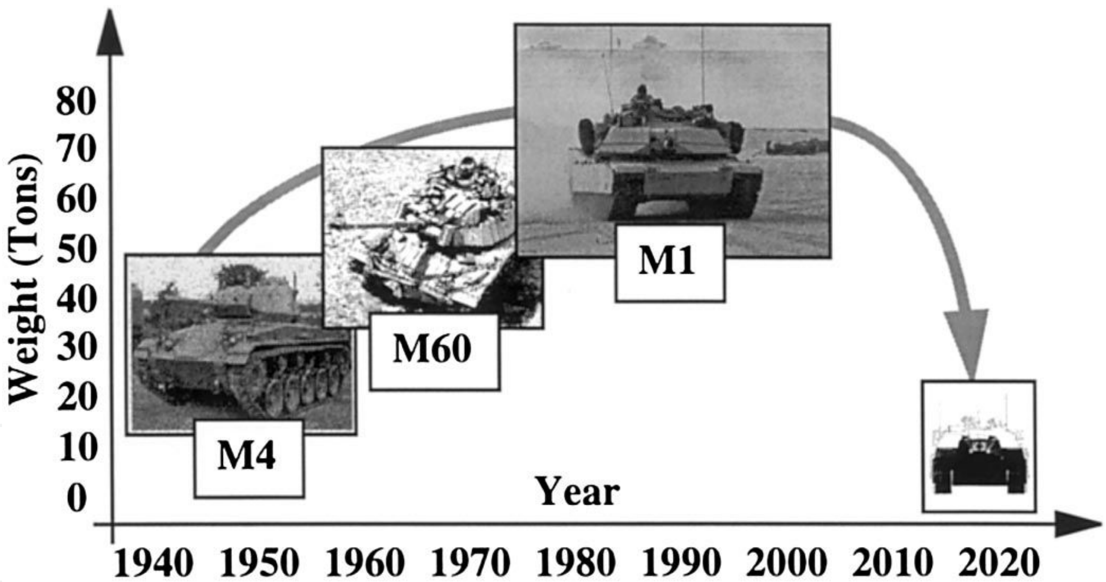

Figure 5. Radical weight reduction for future ground vehicles [65].

At present, the braking system is one of the most important part of the world's transportation systems. The traditional disc brake rotors in use today are manufactured from gray cast iron [72]. Up until very recently, the best candidate material for the future generation replacement of car brake rotors in terms of the relationship between high speed and lower coefficients of friction had not been identified.

The new advances in functionally graded ceramics allows them to be utilized in car braking systems as brake discs. It is anticipated that aluminum titanate **(Al_2TiO_5) FGCs** may replace

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conventional gray cast iron as a result of its better thermal performance when used in car brake rotors. Moreover, due to its low density compared to gray cast iron, **Al_2TiO_5,** it is a fuel saving option for use in car brake rotors [73].

Nowadays, [74] it is known that functionally graded **Al_2O_3/ Al_2TiO_5** ceramics can be used successfully in car brake rotor systems due to the excellent properties and behaviors they exhibit.

5.2. FG ceramics for energy applications

The majority of today's power stations still burn conventional fuels. By optimizing combustion techniques and combining stationary gas turbines with steam turbines, efficiencies close to 60 % have been achieved. The incorporation of advanced material concepts such as FGCs could further improve the efficiency of these systems [75].

Turbine blades made from **titanium aluminide** with gradients in Cr content have been produced by hot isostatic pressing. Measurement of the mechanical properties of machined pieces cut from tested **$Ti_{48}Al_2Cr_2Nb/Ti_{46}Al_3Cr_5Nb_2Ta$ FGC** turbine blades were evaluated after heat treatment at 1350°C for 2 hours, and confirm the presence of the expected microstructural and mechanical gradients [76].

Porous **SiC** FG ceramics are proving to be the most promising materials for use as liquid fuel evaporator tubes in gas turbine combustors with premix burners which can significantly reduce the probability of failure **[77, 78]**. FGCs can also be used as components for integrated thermionic/thermoelectric systems. Figure 6 shows a schematic of a hybrid direct energy conversion system proposed in the second Japanese FGC program [79]. Thermionic conversion is based on the principle that electrons discharged from a hot emitter will move to a low temperature collector located on the opposite side [80]. By applying the FGC concept **(TiC/Mo – MoW – WRe) FGCs**, the performance of the thermionic converter can be optimized by decreasing the energy loss between the emitter and the converter (the barrier index) [79].

Thermoelectric materials with a FGM structure show a higher performance than basic materials. FGC joining is also a useful technique for use in setting an electrode in order to relax thermal stress and suppress inter diffusion. SiGe is one of the materials under consideration for use in thermoelectric conversion at high temperatures. Dense graded SiGe units with electrodes have been manufactured by a one-step sintering process using hot isostatic pressing (HIP) with glass encapsulation, as shown in Figure 7 [81]. Materials with low electrical resistivity, including tungsten, molybdenum disilicide, and titanium diboride **(W, $MoSi_2$, and TiB_2)** were selected for the electrodes. They were blended with silicon nitride **(Si_3N_4)** in order to reduce the thermal expansion mismatch of the joints between the electrodes and the thermoelectric conversion unit.

It has recently been found that the tellurium compounds **Bi_2Te_3** and **Sb_2Te_3** having ZT > 2 and PbTe based FGCs are well established thermoelectric materials suitable for use in the future [82].

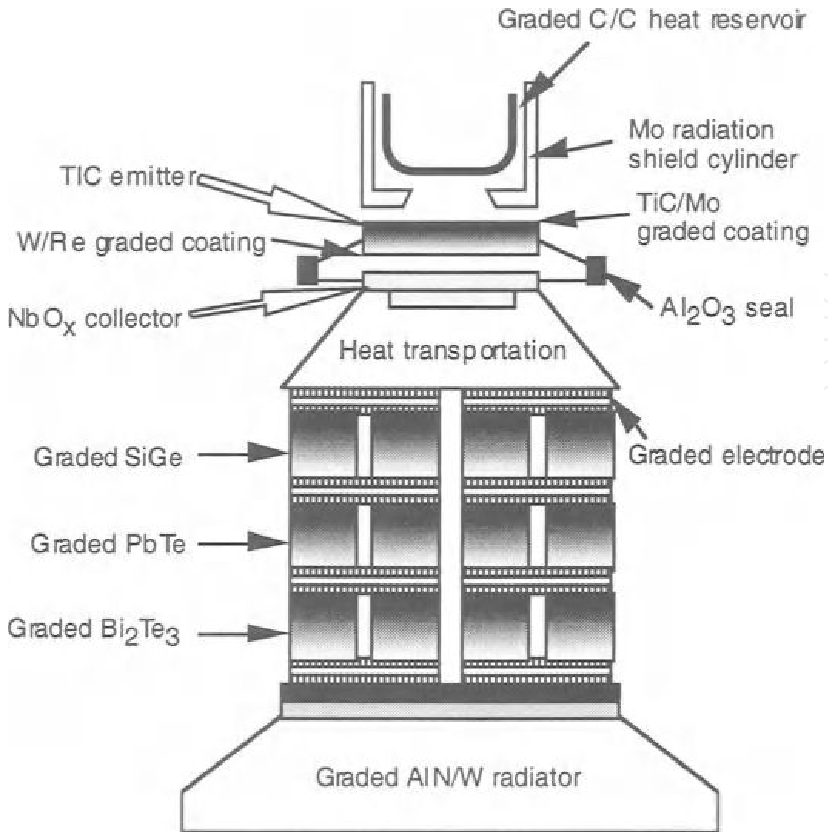

Figure 6. A hybrid direct energy conversion system consisting of thermionic and thermoelectric converters.

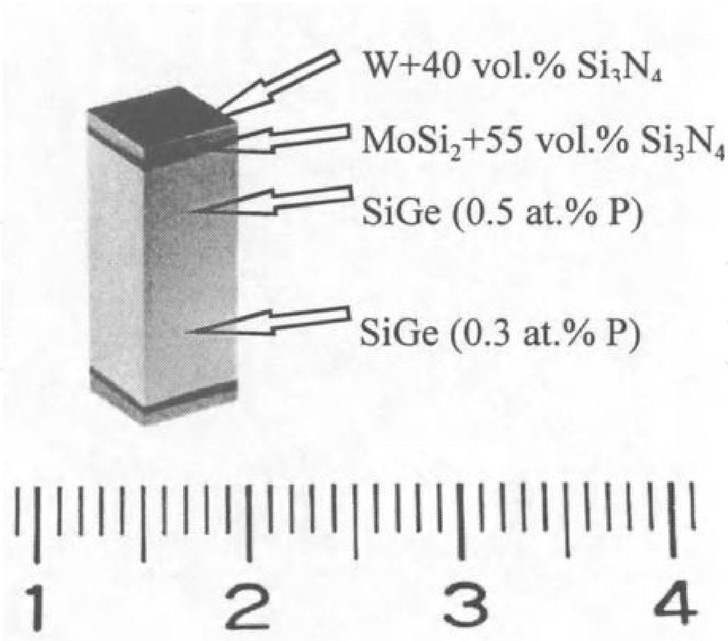

Figure 7. A dense, graded n-type (SiGe) conversion unit produced by HIP [81].

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FGCs are also promising candidates for use in the manufacture of technological components in solid oxide fuel cells (SOFC). [83] has successfully manufactured nano-structured and functionally graded **LSM–LSC–GDC FGC** cathodes to have about 240 μm thick YSZ electrolyte supports using a combustion CVD method. Moreover, FGCs are used as components in the fusion and nuclear reactor field. Chemical vapor deposited FGC coatings of 1 mm thick **TiC/C** were evaluated at a surface heat flux of up to 70 MW/m^2 for several seconds. The FGC film sustained temperature differences as high as 1500°C without cracking or melting [84].

5.3. FG ceramics for electronic and optoelectronic applications

Ceramic/metal and ceramic/ceramic FGMs are showing great promise as both specialized electrical materials, and thermal barrier materials, due to their high temperature properties.

Functionally graded ceramics have become widely and commonly used in many advanced optical and electrical applications such as semi-conductor devices, anti-reflective layers, sensors, fibers, GRIN lenses and other energy applications [85]. In semi-conductors, concentration, carrier mobility, diffusion length, built-in electric field and other properties exert a strong influence on the parameters of electronic and optoelectronic devices. Functionally graded **AlN/GaN** ceramics can be used as a buffer layer for heteropitaxy that is able to distribute strain in the buffer layer and reduce cracking in the active layer [86].

In addition, in conventional edge lasers applied to fiber telecommunications, there are several factors that influence the quality of a device. Two most important are the low threshold current and the numerical aperture of the light beam. It is possible to decrease the numerical aperture, but also to increase the threshold current through increasing the thickness of the active region. One possible solution is the use of a graded-index separate-confinement heterostructure (GRINSCH). In such a structure, the FGC is used as a waveguide cladding layer, and as a barrier to carriers [87].

On the other hand, the substantial shortfall in the efficiency of silicon solar cells is due to the constant band gap width of the bulk material. In such cells, high radiation is absorbed in a shallow layer under the surface. As a result, it is important to initiate an electric field in close vicinity to the surface. A successful way to overcome this limitation is through the use of graded materials [88]. Functionally graded **$Al_xGa_{1-x}N$ (n)/GaN (p)** ceramics can be used as high efficient photodetectors and in solar cells [89].

Piezoelectrics have been used extensively in the design of actuators and sensors in many fields due to their versatility and efficiency in the mutual transformation between mechanical and electrical energy. The piezoelectric actuator has many excellent properties, such as low energy consumption, a compact size, quick response and high resolution. Therefore, piezoelectric actuators and sensors are seen as promising candidates for use in microelectro-mechanical systems and smart material systems. Functionally graded piezoelectric ceramics are novel devices, which can successfully overcome the inherent structural defects in conventional piezoelectric bending-type actuators that result from the use of epoxy binder.

Functionally graded piezoelectric ceramics with a ceramic backing of **(1-x) $Pb(Ni_{1/3}Nb_{2/3})O$/ $xPb(Zr_{0.3}Ti_{0.7})O_3$** are used as highly efficient ultrasonic transducers [90]. These ultrasonic transducers are widely used in ultrasonic measurement systems such as nondestructive testing and medical diagnosis.

Another advanced FGC is porous lead zirconate titanate **(PZT)**, which is manufactured by aqueous tape casting technology and is used in pyroelectric applications [91].

5.4. FG ceramics in biomedical applications

Over the past 30–40 years, there have been major advances in the development of medical materials and this has seen the innovation of ceramic materials for use in skeletal repair and reconstruction. Bioceramics are now used in a number of different applications throughout the body. However, the increase in biomedical applications of bioactive ceramics is occurring simultaneously with the growth of interest in tissue engineering.

The use of FGCs in biomaterial applications is growing in importance. Over 2500 surgical operations undertaken to incorporate graded hip prostheses have been successfully performed in Japan over the past twelve years. These graded hip implants enable a strong bond to develop between the titanium implant, bone cement, hydroxyapatite (HAp), and bone. The bone tissue penetrates HAP granules inserted between the implant and the bone forming a graded structure. Hence, FGCs have enabled the development of this promising approach to bone tissue repair [92].

Biomaterials must simultaneously satisfy various requirements and possess certain properties such as being non-toxic, having good mechanical strength, and they need to be biocompatible [93, 94]. Natural tissues often possess FGMs which enable them to satisfy multiple requirements [95]. Human tissues have evolved to be best adapted to their multiple functional requirements. For instance, the perfect design of natural bone with a dense, stiff external structure (cortical bone) and a porous internal structure (cancellous bone) demonstrates that functional gradation has been utilized for biological adaptation [96].

A functionally graded carbon fiber (CF) reinforced poly-lacticacid (PLA)/nanometer hydroxyapatite (HA) biomaterial has been prepared by [97]. CF was used as the reinforcement to improve mechanical properties, while at the same time the advantages of PLA and nano-HA were retained. [31] developed a dental implant with functionally graded titanium (Ti) and HA. [98, 99] developed a functional gradient HA composite containing glass-coated Ti and studied its microstructures, mechanical and thermal properties. [100] proposed a **HA–glass–titanium (HA–G–Ti)** composite and implanted it in the femur of a dog to evaluate its bonding strength. However, metal and polymer-based implants usually lead to stress shielding, wear debris, delayed osseointegration, resorption, degradability or other biological complications. Therefore, new bone tissue implants should aim to avoid these disadvantages and instead meet the multiple functional requirements of bone tissue [101, 102].

It was found that calcium phosphate ceramics, especially the bioactive nano-structured hydroxyapatite, have received considerable attention in recent years [103–105]. In vitro and in vivo experiments have demonstrated that the nano-HA has an excellent biological performance when compared with conventional micro-grain HA [106, 107]. Nano-HA possesses exceptional biocompatibility and bioactivity with respect to bone cells and tissues. Hence,

[108] prepared a successful nine layers of laminated and functionally graded HA/ yttria stabilized zirconia (Y-TZP) for orthopedic applications, using an SPS technique.

In addition, [92] presented a novel FGC with both micro-grain and nano-grain HA crystals that is able to satisfy the mechanical and biological property requirements of bone implants. It was concluded that a biologically functionalized nano-rough surface contributed better bioactive functionality to the HA ceramics. By applying the concept of FGM, bio-inspired multifunctional biomaterials open the door to a promising approach to bone tissue repair.

Other functionally graded ceramics that are used in biomedical applications are **ZrO_2/AISI316L** as artificial joints and hip prostheses, and **ZrO_2/Al_2O_3** FGCs as teeth implants [109]. Nowadays, structure grading technology is also used in cancer prevention research. One of them, for instance, is a study on collagen structure reinforcement using grading technology. In such a type of graded structure, the graded material should not only possess excellent hardness, wear and corrosion resistance, but should also have high biological compatibility and harmlessness.

5.5. FG ceramics in structural and tribological applications

FGCs offer great promise for use in applications where the operating conditions are severe, for example, in cutting tools and wear resistant linings for handling large heavy abrasive ore particles. These applications require graded ceramics with high corrosion and wear resistance. This type of FGC can also be used as protective coatings in the form of an **alumina/mullite FGC** that is used to protect SiC components from corrosion, and act as a thermal barrier coating, improving the efficiency of turbine engines by providing the capability to sustain a significant temperature gradient across the coating **ZrO_2/Al_2O_3** FGC, which also improves thermal resistance and resistance to oxidation [110].

Moreover, a novel functionally graded **Al_2O_3/lanthanum hexaaluminate (LHA)** ceramic with a gradient in composition and porosity was developed using the PM method as a high temperature thermal barrier coating, protecting the components from a corrosive and severe thermal environment [111]. Graded **WC/Co FGCs** are used as abrasive cutting tools and in mining equipment, where a high wear resistance and toughness are both required [112].

In addition, the WC/Co FGC is coated with a layer of titanium nitride **(TiN)**, a layer of alumina **(AI_2O_3)**, and a layer of titanium carbonitride **(TiCN)** by chemical vapor deposition. These graded and multiple coated WC/Co FGC cutting tool chips are very resistant to flank wear. Furthermore, they have the advantage of a high machining speed combined with a high feed rate. Their graded composition can also control the internal stresses arising from the mismatch in thermal expansion. A simple, asymmetric gradient in composition such as in a ceramic/metal FGM can reduce thermal stress, while a symmetrical or radial gradient can induce a sizable compressive stress at the outer ceramic layer, resulting in stress reinforcement similar to that of tempered glass or pre-stressed concrete [113]. Graded cutting tools have also been made for interrupted cutting from cermets of **TiC-NiMo FGC** in which the percentage of TiC in the graded layer ranged from 95 wt. % at the top surface to 86 wt % at the site of transition to plain steel [114]. Recently, **Al_2O_3/TiC** and **Al_2O_3/(W-Ti) C** FG ceramics have been investigated as highly efficient ceramic tools with excellent thermal shock resistance [115].

FGCs are also used as engineering components, machine parts and in joints for gas and steam turbines as well as in coatings and wear resistant materials [116]. For example, **SiC/C** FGC acts as a structural part of the heat collector for an energy conversion system, and also provides thermal stress relaxation, heat conduction, and protection from oxidation.

Another FGC application that involves thermal stress relaxation and a low coefficient of friction, is in welding apparatus. For example, **Si_3N_4-Cu FGC** is used in automated electric arc welding of the large aluminum sheets used in building huge ships such as liquid natural gas (LNG) tankers [117]. Other suggested applications included use as filters, catalysts, mufflers, heat exchangers, self-lubricating bearings, silencers, vibration dampers, and shock absorbers [118].

Silicon nitride Si_3N_4, and silicon aluminum oxynitride **SiAlON** are a special class of high temperature ceramic and refractory materials. Moreover, they represent a vital and unique class of structural ceramics. They can be used in many industrial and structural applications that require chemical stability, high heat resistance and specific mechanical properties [119].

Previously, [120] developed graded in situ SiAlON ceramics by embedding **β-SiAlON** green compacts in **α-SiAlON** powder. The compositions, microstructures and properties of the graded SiAlON ceramic change gradually from the hard α-SiAlON with spherical morphology on the surface, to the tough and strong β-SiAlON with elongated grains in the core. [121] developed a technique for the in situ formation of an α-SiAlON layer on a β-SiAlON surface. In another study, [122] obtained a gradual change of α-SiAlON content from the surface through to the core using the rapid cooling method. Recently, [123] have manufactured a twin layer FGC of **α-SiAlON (100 wt%)/AlN-BN (50:50 wt%)** for advanced structural applications.

5.6. Other applications of functionally graded ceramics

In addition to the above mentioned applications, FGCs can be used in the lining of thermal furnaces and other ultra-high temperature applications:

- Novel **zirconia-mullite/alumina** FGC tailored by the reaction sintering method and used in refractory materials that line furnaces, and high temperature applications [6, 7].
- **ZrB_2/ZrO_2** FGC prepared using spark plasma sintering for ultra-high temperature applications and in severe environments [124].
- **ZrO_2/Fe** FGC with excellent thermal and mechanical properties, used for high temperature engineering applications [125].
- A crack-free **Si_3N_4/Al_2O_3** FGC suitable for high temperature structural applications [26].
- Multi-layered Zircon/yttria **(ZrO_2.SiO_2/Y_2O_3)** FGC with high thermal shock resistance, used as crucibles for the induction melting of TiAl based alloys with zero contamination [126].

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6. Future direction

Functionally graded ceramics are excellent advanced materials with unique properties and characteristics that have entered into the manufacturing world in the 21st century. The major success of FGCs is due to the fact that the irreconcilable properties on each side of a FGC can be fully utilized. FGCs can be tailored according to the application requirements by controlling the appropriate components in order to achieve some specific tailored applications and to overcome the problems of laminated composites. However, there are some obstacles to the realization of this success. The high costs that are entailed during the manufacturing process and powder processing are considered to be a crucial issue. The technology of powder metallurgy can offer a vital solution to this problem, however, there are a lot of issues relevant to this technology that need to be considered. In addition, an extra effort in different axes should be exerted in order to generate a predictive model for proper process control. This will improve the execution of the process and so reduce the cost of FGC production. Another issue that needs to be taken into consideration is that of determining the residual stresses resulting from the inhomogeneous cooling of the graded layers of the FGC body. The values of these residual stresses are an important indication to both the success of FGC preparation and to their subsequent properties. Because one of the main purposes when designing FGCs is to decrease or prevent the residual stress formed at the interface of the two dissimilar materials, and thereby prevent crack propagation and ultimately the delamination of these materials by having smooth transitions between layers.

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