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Functionally graded materials manufacturing techniques: A review

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ABSTRACT

Functionally Graded materials (FGM) are multifunctional materials which are used to produce components that require functional performance which is variable within the component and this functional performance is achieved by manipulating the composition either at micrometer level or at nanolevel. This is basically termed as engineering the transition in micro/nanostructure. This in fact enhances the overall performance of the component. These materials are currently in the forefront of material research. Numerous techniques have been proposed in the last two decades and practically exercised for manufacturing of FGMs. This article presents a comprehensive deliberation of powder based manufacturing techniques which have been employed by the researchers throughout the globe for successful fabrication of an FGM. Attempt is made to throw light on practical applications of FGM and on few important issues while attempting for FGM synthesis. The work reviewed in this paper is mostly confined to the significant powder based manufacturing techniques, application areas and elementary issues, addressed with regard to FGM synthesis in the last ten years. Earlier articles are omitted unless their inclusion is necessary for the understanding of the subject. Effort is made to discuss various significant metal/ceramic combinations used for FGM synthesis.

KEYWORDS

FGM;
Powder Metallurgy;
Electrophoresis;
Electromagnetic separation;
Laser Technologies.

INTRODUCTION

Human civilization has always tried to create things as per its own criteria and thus suiting and soothing their needs from centuries. One can visualize the evolution in all areas of technological development and can have a feel how the gradual development has taken place. One area which has always been in human minds is of the area of materials. The findings of archaeology reveal that human civilization has been using metals since the Neolithic period and mining and working of metals began in around 8,000 B.C. From metals to alloys and then to composites and then Functionally Graded Materials (FGMs), there has been consistent and drastic progress in the area of material science and engineering.

FGM is a unique concept first realized and attempted by Japanese in the Sendai area of Japan in 1984 with a specific intention to create a material which can with stand high thermal barrier[1]. The idea behind this exercise was to create a material which can withstand extreme temperatures on one side and have better thermal conductivity on another side by continuously tailoring the composition of the material at micron level. Initially only few methodologies namely chemical vapour deposition/ physical vapour deposition (CVD/PVD), powder metallurgy, plasma spray and self propagating combustion synthesis were implemented to attain the transition in composition and structure. Kawasaki et al. 1995 has given a comprehensive review of powder metallurgy based fabrication of functionally graded material but being a very easy and viable route this technique is expensive and fails where step-less gradients are required[2]. However, the emphasis in the last decade is to develop techniques which have low cost, good reproducibility and take less time to produce FGM. The structure, composition and morphology variation hold the key to creation of an FGM[3]. The gradual shift or variation can be predesigned and an intentional tailoring is introduced to achieve desired functionality as per the requirement of the application[4]. This outstanding capability separates the FGMs into a distinct category of materials and places them uniquely when compared to metals, alloys and composites. The current review focuses on some significant manufacturing techniques developed so far for manufacturing of FGM. An attempt is made to present briefly the various fundamentals of powder based FGM preparation techniques. Further the important material combinations used for FGM preparation till now in various techniques are also discussed.

Nomenclature

F_e	Electromagnetic Archimedes Force
σ_1	Electrical conductivity of melt.
σ_2	Electrical Conductivity of primary particle.
d	Diameter of primary particle.
J	Current Density.
B	Magnetic Flux Density.
C_d	Coefficient of drag.
ρ_1	Density of primary particle.
ρ_2	Density of melt.
F_b	Buoyant Force.
g	Acceleration due to gravity.
F_d	Drag force.
v	Particle velocity.
v_t	Terminal velocity.

Strategy for FGM development

The complete strategy for FGM development involves two discrete steps. The first step is to focus on chemical composition & microstructure/nanostructure manipulation as per desired properties to achieve the desired functionality in the material as per service requirement. The second step incorporates the role and realisation of manufacturing strategy to create such FGM, with fine reproducibility. In nut shell it is proposed that a FGM is created if there is precise control on chemical composition and fabricabilty exists for such material. It can be said that FGM creating is integration of above cited two steps. Kieback[5] gives a very acute definition of FGM creation: 'the manufacturing process of FGM can be divided in to two simple steps: "Gradation" i.e. building the spatially inhomogeneous structure and "Consolidation" i.e. transformation of this structure into a bulk material'. The final accomplishment of such a task is not that simple, in fact it needs more. In order to commence for FGM Development it is essential to have a wide database of properties of various materials for different chemical compositions say Young's modulus, coefficient of thermal expansion, Poisson's ratio, thermal conductivity etc. Once this knowledge is available the design of FGM is to be proposed by the designer keeping in mind the need of application area. It can be termed as a kind of proposal for optimizing the material properties in one or other way. However, this is to be done carefully by experimenting and subsequently analysing the effect of microstructure on properties[6]. After preparing FGM it is evaluated using standard test procedures and the results are again stored in the database thus enriching the content of the database so as to use this data for future when using the same or different material combination. Hence it is established that FGM creation is an iterative process in which FGM created is tested for properties for which it was designed and the focus is always on to reduce the gap between the design expectations and ultimate properties found by testing the manufactured FGM. This iterative process is just a replica of feed back loop of Control

Engineering where the intended and attained are compared by analysis and further improvements are suggested and implemented till a FGM with desired functionality is achieved in reality.

MANUFACTURING TECHNIQUES OF FGM

As of today there are more than forty techniques available for synthesis of FGM. An old classification of various techniques of FGM based on material phases viz. solid, liquid and gas is given by A. Kawasaki,[6] however, with rapid development in the manufacturing of FGMs and evolution of manufacturing strategies in last decade it is difficult to stick to this old classification. There are techniques where more than one phases are involved. Another classification based on methods for the production of FGM has been given in an excellent treatise on FGM by S.Suresh et al.[Fundamentals of FGM by S.Suresh & A. Mortenson] ten years back and still hold good. They classify the production methods of FGM in two categories: Constructive Processes & Transport Based Processes. In this article few significant techniques which a beginner in the area of FGM must be acquainted with are covered. The various techniques are classified as:

(i) Powder Metallurgy Based methods
(ii) Electromagnetic/Electrophoresis based methods.
(iii) Laser Assisted Technologies and
(iv) Others.

We shall go into the review of these significant techniques consecutively throughout this article.

Powder metallurgy (P/M) based methods

Powder metallurgy is the one of the simplest, fast, elegant and economic technique for manufacturing a FGM. It is capable of producing a gradient either in a continuous manner or in a stepwise manner[7]. The P/M approach is capable of producing layer thickness of medium (100-1000 micrometer) and large (greater than 1 mm thickness) and bulk FGMs with very good versatility in phase content can be produced[8]. The powder metallurgy technique can create FGM of a metal and ceramic combination; however glass-ceramic FGMs have also been reported[9]. In such a combination, the step wise gradient can be achieved by commencing from a pure layer of either a metal or a ceramic or vice versa with intermediate layers of both metal and ceramic and finally terminating at either a ceramic or metal layer. It should be assured at the same time that mutual diffusion of constituent phases must be negligible. The continuous gradient is achieved by intentional gradual blending of mixture of metal and ceramic. The powder perform thus formed is then densified by conventional established methods of Material science and engineering. The generalised flow diagram of a P/M based FGM preparation is shown in Figure 1.

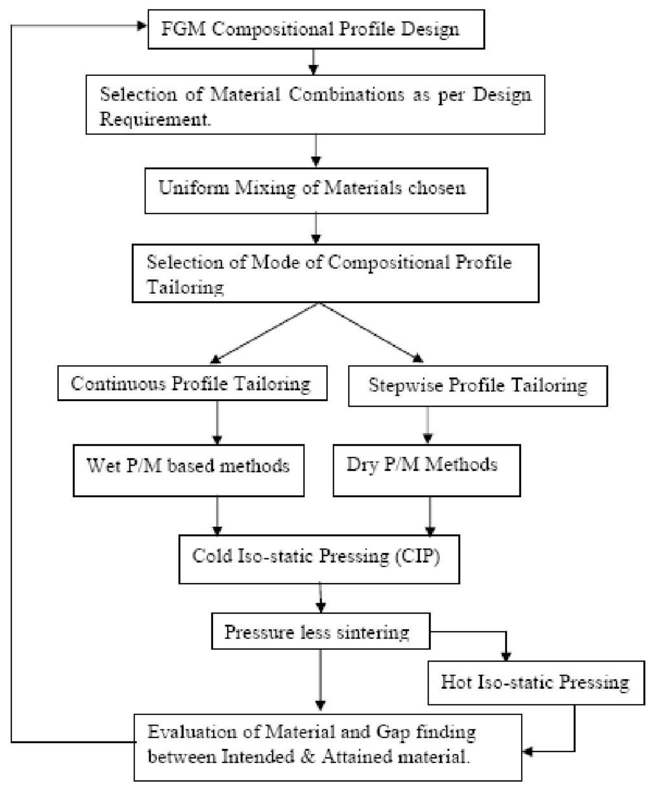

Figure 1 : Generalised Flow diagram of a P/M based FGM preparation

The powder metallurgy process involves selection of an appropriate combination of materials as per design. Once the material combination is decided the starting powders in different ratio are first blended using a Ball Mill. The next step is to make a decision as in what way the profile is to be blended at micron level. If a continuous profile is required, the wet P/M approach is usually applied while if stepwise profile is required the dry P/M approach is applied normally. The various approaches which fall under wet P/M category are wet powder spraying[6,10], slip casting[11], centrifugal casting[12-16] The wet P/M approach normally requires binders for stabilization of green bodies, various techniques like centrifugal processes powder spray forming etc are potential methods in this approach. In powder spray forming, metal suspension and ceramic suspension in ethanol or any other suitable organic binder are sprayed using a spray nozzle but the content of such a binder has to be eradicated before going for sintering at higher temperatures.

The dry P/M approach is less intricate as compared to other techniques. This involves stacking of different layers of mixture of powders mixed in different proportion. This process is usually done in a die where layers of powder stacks are manually placed ensuring uniform thickness and distribution of powders in every single layer. This process can be regarded as a constitutive process which builds the gradation of material. Once this step is over a pre compaction process is carried out after extracting the green from this die to attain a green compact. Researchers have used Universal Testing Machine for unidirectional compaction along the thickness direction[17]. After pre-compaction the cold isostatic pressing is done followed by sintering process, which is basically a consolidation process. The process parameters for such a process must be chosen in a way that gradient are not altered from the desired one[5]. The sintering of such compacts is a sensitive issue and to be done with utmost care as ceramic and metal in a ceramic-metal combination exhibit different sintering behaviours[18]. At the same instant because of difference in sintering rate of most of metal and ceramics, it becomes difficult to attain uniform sintering rate throughout the compact. The sintering behaviour is definitely affected by various other parameters like powder particle grain size, compositions and porosity of the mixtures in use[19]. Effort should be made to choose a combination such that the difference in Coefficient of Thermal Expansion (CTE) is less, resulting in nominal generation of thermal residual stresses at the interfaces, reduced warping, splitting and cracking[20].

The last process of the flow diagram (Figure 1) is the evaluation of what has been manufactured and how far it is from initial compositional design. Once this gap is minimized we can claim a FGM with desired designed functionality is obtained in reality.

Significant metal/ceramic combinations fabricated via P/M route

A number of combinations have been tried by various researchers for preparation of FGM. A combination of powders of Mullite and Molybdenum in ethyl alcohol was produced by Tomsia et al. where they produced FGM cylinders of about 15 mm by pressure slip casting[20]. However they claimed that it is not advisable to attempt for FGM preparation using water based slurries as the ultimate product they achieved was homogeneous mullite/Mo composite. Their work produced FGM with both conductive and insulating areas. Bartlome et al. has again used the same combination but the focus of this work was to evaluate the processing, mechanical properties and micro structural properties[21]. They compared three differently designated Mullite/Mo combinations and their work can be considered as superior to the work of Tomsia et.al. Gang Jin et al. used this combination recently in 2005[22]. They analysed both mechanical as well as thermal properties of this combination. Prior to them the thermomechanical properties of Mullite/Mo FGMs were not investigated in detail. They used pulse electric current sintering for sintering of compacts.

FGMs also have promising bio-medical applications in orthopaedics and dentistry[23-30]. Hydroxyapatite (HA) which has chemical formula $Ca_{10}(PO_4)_6(OH)_2$, is commonly found in the teeth and bone of human body and is used as a substitution material to replace amputated bone or as a coating to promote bone in growth into prosthetic implants. The bending strength and fracture toughness of pure HA is around 36.89 MPa and 0.663 MPa which is very less as compared to that of human bone and so using pure HA is not advisable for heavy loaded implant applications. Chu Chenglin[31] produced a bioactive FGM for applications in hard-tissue implant with a combination of hydroxyapatite and Titanium i.e. HA-Ti by an optimized powder metallurgy process. The same combination was used by Bishop[32]. The work of Bishop was purely on production and macrostructure of FGM with this combination and critical properties were not analysed, however C.Chenglin optimized the fabrication procedure, analysed microstructure, phase constitution, density & mechanical properties and finally the fracture behaviour was also discussed in his work. They claimed that fracture behaviour varies with the rise of Ti content and is controlled by Ti matrix in Titanium rich region and presents quasi-cleavage fracture with many tearing edges. S.Katkam et.al[33] fabricated a functionally graded material of HA and Ag_2O using a domestic microwave oven and the samples were sintered in the domestic oven itself and the results were compared with conventionally sintered FGMs. The top layer of the FGM they prepared was having some metallic silver with HA and tricalcium phosphate (TCP) which is known to be a bioactive material while the middle layer was having increased content of HA with TCP and little traces of silver. The methodology adopted was inspired from the work of Kon and Ishikawa[34] where instead of spraying silver oxide, diamond powder was sprayed. Watari and his colleagues at school of dentistry in Japan performed a novel experiment by inserting Ti, Ti/20%HA and Ti/30%HA FGMs into femora of rats to evaluate the biocompatibility of the material they made by cold Isostatic pressing and sintering[35]. They reported enhanced biocompatibility and no inflammation were observed in the stipulated implantation period. Further in 2004[23] they again used various combinations for preparing FGMs and concluded that gradation of material in turn produces the gradation of tissue reaction when the implant prepared by FGM is induced realistically into the living body. This established the fact that the tissue response can be controlled by Bio-FGMs.

Fabrication of ZrO_2-NiCr FGM was attempted by Jingchuan Zhu[36] by hot pressing and the resulted FGM was critically analysed for mechanical properties like hardness and bending strength. This work exhibited how the mechanical properties vary corresponding to constitutional change; in fact they successfully produced ceramic and metal alloy combination and were able to achieve almost two fold increases in bending strength as compared to pure nickel which is 330 MPa. This combination was also taken later by J.Q Li[37] with an intention to understand the behaviour of FGM constituted of above said materials under thermal cycles up to 1000 ^{0}C. They came up with the conclusion that increasing the thickness of the interlayer certainly improves the capability of Metal-Ceramic rich interlayer to resist crack formation and even if the cracks are formed they grow at very slow pace in further thermal cycles.

Ma and Tan used a combination of Ti and TiB_2. They investigated the effect of starting powder particle size on mechanical properties and also came with few conclusions regarding sinterability rate of this material combination when the starting powder particle sizes were different[18]. It was found in this work that smaller particle size improves the densification of TiB_2 ceramics however if the sintering temperatures and pressure are kept low the effect of particle size is not that much significant. SiC proved to be a sintering aid and resulted in the increased flexural strength and toughness of this FGM. They have also successfully reduced the porosity of TiB_2 layer by adding a layer of SiC and thus avoiding the oxygen contamination, in fact they claimed a reduction of porosity by 10 % which in turn is an indicative of increase in relative density and subsequently the bending strength.

Machinability of materials is another issue, particularly speaking of ceramics which are used in structural applications. The conventional machining is highly intricate and sometimes result into failure of ceramic materials, an option is to manufacture a FGM whose some part can be machined easily and remaining part shall retain the other properties of ceramics like strength, hardness and fracture toughness. Wang and his co authors[38] have developed a new design method for manufacturing such ceramics and their research has developed a graded machinable ceramic with material combination of Si_3N_4/h-BN and Al_2 O_3/$LaPO_4$. Instead of mixing the two powders as per predesigned profile (which is a usual practice) their design profile was different in a way that they used a core layer of one material and subsequently mounted layers of another material purely in different proportion on either side of the core layer. This method can be called as bidirectional unicomponent gradient distribution. This attempt resulted in enhanced machinability and fracture toughness.

S.Lopez-Esteban[39] investigated a different aspect of FGM Preparation when they tried to control the rheology of the suspensions with starting powder mixtures. They claimed that ultimately the shape profile of FGM they prepared of Zirconia and stainless steel is dependent upon the combination of sedimentation velocity of metal particles and ceramic particles and drying of slurry.

L.YongMing[40] used the same predesigned compositional profile as used by C.Chenglin[31] for $Ti_3 SiC_2$ and Alumina. Alumina being a potential material in applications where high wear conditions dominate or high heat resistance is required. It lags where high toughness is also an additional functional requirement. Titanium carbide is easily machinable and is conductive electrically as well as thermally. Hence a combination of such materials is definitely a good idea for use in applications where all above functional features are needed in a material.

Attempts have also been made to fabricate FGM using high melting point silicides of Niobium. E.M Heaian et al.[41] have synthesised dense graded Nb/Nb_5Si_3 composites using elemental powders of Niobium and Silicon. They used a custom built apparatus for fabricating their FGMs and claimed the enhancement in fracture toughness with increase in content of Nb. Such an FGM opened wide horizons for use in high temperature structural applications.

FGMs have also been reported for Plasma Facing Components (PFCs) in nuclear fusion reactors[42-45]. PFCs consist of a plasma facing and a heat sink material. They are exposed to high heat and high neutron flux generated by plasma. SiC/C combination is an ideal when one has to fabricate an FGM for such use. Graphite has stability under high temperature conditions and has excellent thermal conductivity, but at the same time it has a tendency to retain tritium and sputters and sometimes sublimes due to irradiation. SiC has excellent high temperature properties, corrosion resistance and so a combination of these two can match the requirements of an ideal PFC. Chang-Chun ge et al 2000[42] attempted various combination for PFCs like SiC/C, B_4C/Cu and W/Cu, their results showed promising applications of these combination as PFCs. Y.H Ling[43] developed a different combination of Sic/Cu and their tests reported less chemical sputtering than the combination previously used. A.H.Wu and his co-workers[46] produced Si/C FGMs which were suitable to be used as first wall materials for fusion reactors. They also checked their samples for thermal fatigue and claimed that they did not detect any micro-crack and flaw under hundred times plasma erosion conditions. The thermal shock resistance was also reported to be higher that monolithic SiC ceramic. Sakamoto at al. and N.Sakamoto have done the developments of a bonding technology of Beryllium and copper alloy which are used in the divertor components with FGM inter layers. They claimed from their results that Be-Cu sintered compacts having more than 50 at% Cu were advantageous for the application as FGM interlayer. A stainless steel/ceramic/stainless steel FGM has been developed by S. Nishio et al. in 1996 for integrated insulation joint of the piping system in fusion reactor environment. They were successful in suppressing the residual thermal stress generated in the sintering process.

Two another metal ceramic combinations were studied by M.Bhattacharyya et al.[17]. Three FGM samples of Al/Sic and Ni/Al_2O_3 were prepared, however the number of layers were varied from 2 to 5. The peculiarity about this work is instead of traditional approach of varying the metal/ceramic content from one layer to the last layer i.e. metal content 100 % at first layer and then gradual decrease in metal content and consequent rise in ceramic content and attaining 100% ceramic content at last layer, the compositional gradient was fixed as 100% at top layer as usual but in a two layered sample the second layer was made to be a 60/40 layer. In the similar fashion for other FGM samples the last layer was always having 60/40 layer however intermediate layers were varied. It was verified in this work that increasing the number of layers results in decrease of porosity of such FGM systems. These samples were having increase in micro-hardness as and when the increase of ceramic content took place. They also explained beautifully how the effective flexural strength also increased with the number of layers under mechanical & thermal loading for both combinations and summarised this work by comparing the bulk and interfacial properties of FGMs they prepared.

One ever existing challenge when fabricating FGM had been as to how to eliminate cracks and camber in the resulting FGM samples. If there is a significant difference in sintering behaviour and CTE of two constituents of FGM, the resulting FGM samples will definitely not have continuous, defect free interface profiles. The recent work of Li Sun et al.[47] gave an insight to the new researchers in the field of FGM preparation. Reports exist in literature regarding the reasons behind such happening of defects but significant works so as to eradicate this problem are few. Li Sun studied[47] two important characteristics for a material combination of alumina and Zirconia powders like packing density of contents and particle size distribution and explained how these two characteristics affect the overall comapcatibility of green samples. In fact it is much needed to say that the powder characteristics play an important role in reducing the possibility of crack generation and camber; there definitely exist a proper proportion of constituents for which the shrinkage will be minimised after sintering of the sample in each layer. Another factor which cannot be neglected is the shrinkage rate of powder constituents of an FGM sample during sintering; if the shrinkage rate of the powder constituents is same the possibility of crack formation and camber is definitely reduced to a significant extent[48].

Electrophoresis/ electromagnetic based routes for FGM preparation

Electrophoresis and Electromagnetic separation are two significant and latest emerging techniques of FGM preparation. In current scenario of FGM research they are attaining wide popularity because of their simplicity and low expenditures incurred when attempting to manufacture FGM.

Basic principles of electrophoresis based FGM manufacturing

Electrophoretic Deposition is a very well known electro-kinetic phenomenon based on the theory of electrophoresis and has certainly drawn attention as a simple and elegant technique for FGM synthesis in recent years. This phenomenon was first noticed by an Indian researcher named G.M Bose while studying liquid-siphon experiment in mid eighteenth century; later Reuss (1807) deliberated the details of this phenomenon in his famous Double layer theory[52].

The typical aspect of this phenomenon is though it is implemented successfully still there are numerous theories associated to this phenomenon like particle charge neutralization by Grillon[49], electrochemical coagulation of particles by Koelmans[50] which was an extension of DLVO (Derjaguin-Landau-Verwey-Overbreek) theory and particle accumulation by Hamaker[51] etc.. However we shall go into the details of this phenomenon by Double layer theory with the help of the Figure 2.

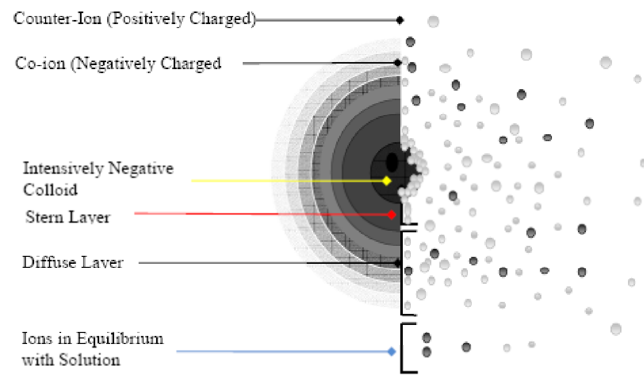

Figure 2 : Double layer theory details

Let us visualize that in centre there is a highly negatively charged colloid present, this highly negative colloid will attract the counter-ions(positive ions in this case) from the solution and as a result a firm layer of such ions will be formed around the surface of the colloid, this layer is called as stern layer. More counter-ions will tend to move towards the centre but they are now repelled by layer of counter-ions. As a result a dynamic equilibrium will be established and this ultimately will result in to the formation of a diffuse layer of counter-ions. The concentration of counter-ions will be highest near the surface and slowly decreases with distance till equilibrium is established with counter-ions in the solution. Similarly, it is obvious there is lack of co-ions(negative ions in this case) in the vicinity of the surface as they experience repulsion by negative colloid. The concentration of such particles slowly increases with distance, as the repulsive forces of the colloid are screened out by counter-ions. The layer of strongly attached counter-ions and the charged ambience of diffuse layer together are called as Double layer.

Electrophoretic Deposition requires a stable suspension to begin with however the particles must be charged so as to respond to an applied electric field[52]. An EPD set up usually consists of two suspension chambers and one deposition chamber. The first suspension chamber is usually named as circulating suspension chamber and has well defined quantity of first suspension which we call as circulating suspension while the second chamber is called as chamber with added suspension. The suspension which is initially in the circulating suspension chamber is pumped to deposition chamber. The deposition chamber has electrodes with defined surface area and distance between them. In the mean while the second suspension is added to circulating suspension chamber so as to vary the concentration of the content in the circulating suspension chamber. Varying the pumping rate varies the composition of the FGMs thus made by this process. The flow diagram of an EPD process is shown in Figure 3.

The various parameters which are significant and must be taken care for Electrophoretic deposition are

(i) Particle size: The particle size is very important as the large particle size can result into sedimentation during EPD process[53]. The preferred particle size is less than 10 micrometer. However, one important aspect of EPD is that deposition rate is independent of particle size which makes it a facile technique for FGM synthesis.

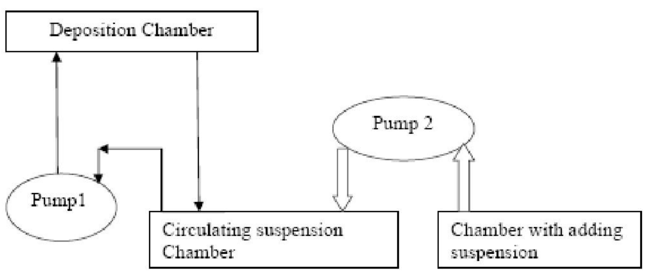

Figure 3 : Flow diagram of an operational EPD cell

(ii) Point of zero charge (pzc): The pzc is that p^H of the suspension when the powder particles carry no net charge and then only the stability of a suspension is said to be attained. So far the method of potentiometric titration is preferred to find pzc of a suspension. Stable suspensions provide a dense, homogeneous deposit without traces of flocculation and don't result in low density deposits during EPD.

(iii) Natural p^H of powder: The natural p^H of a powder is the value for the suspension in equilibrium, when a specified quantity of powder is suspended in a demineralised water (p^H=6) at a given powder concentration (differing from experiment to experiment). This dictates the choice for suspension medium to be used for EPD process.

All above parameters are very closely interrelated and dictates the choice of suspension medium in EPD. When the natural p^H is greater than pzc, the powder is negatively charged and when the natural p^H is less than pzc, the powder is positively charged. In the first case the alkaline suspension is needed while in later acidic suspension is suggested for use. Another parameter which is to be kept in mind is the value of suitable voltage which is to be used for EPD. At voltages above 3 V it was suggested by S.Put and his co-workers[53] that organic based suspensions are to be used. The detailed schematic diagram of an EPD process is shown in Figure 3

Significant material combinations used for FGMs via EPD route

Kawai et al.[54] have produced C/C & SiC FGM using electro-deposition method where they claimed to achieve the compromise between specific strength and oxidation resistance by gradation of matrix composition and the resulting FGMs were having approximately two fold enhancements in both the properties. Sarkar and Dutta[52] have examined the EPD process in detail citing different theories and proposed and alternative explanation for EPD process using DLVO theory and lyosphere thinning. They had been successful in preparing a wide variety of FGMs using viz. Al2O3/YSZ, Al2O3/MoSi2 and others.

Few other significant works in this technique are to the credit of S. Put and his fellow workers. They prepared functionally graded WC-Co materials of 35×35 mm with a thickness of about 2mm, in which the gradient layer was as small as 1.5 mm. One interesting finding in their work was that in an exercise to obtain full densification, when the sintering of samples was done at around 1400 ^{0}C the gradient disappeared completely and resulted into homogeneous materials. Apart from this finding it was also observed that enhancing the addition rate of suspension in EPD process results in steeper gradients. In same continuation Put and his team[55] developed an EPD model for prediction of composition gradient for FGMs in the green deposit as well as in the sintered material. This model was quite satisfactory and there was a good compromise between the predicted and actual gradient obtained. It can be said that this model developed by them is very much up to the mark with the spirit of FGM synthesis where it is always required to reduce the gap between the design and actual material obtained after synthesis. A tabular summarisation of various FGMs fabricated via EPD with significant results by various researchers in last fifteen years is given in TABLE 1.

TABLE 1 : Significant Materials Combinations via EPD

S.No.	Material combination of FGM	Nature of Gradient attained	Range of Content Variation	Range of Hardness variation	Sintering Conditions	Author	Year
1.	YSZ-Ni	Step	One side 100% YSZ & other pure Ni	13.5 G Pa to 1.35 G Pa	1300 C hot pressing	P.Sarkar	1996
2.	Ni-Al2O3	Step	One side 100% Al_2 O_3 & other pure Ni	Not Reported	Vacuum Sintering at 1420 C	P.Sarkar	1996
3.	MoSi2-Al2O3	Step	One side 100% Al_2 O_3 & other 60 v/o $MoSi_2$	Not reported	1800 C in Vacuum for 3 hrs	P.Sarkar	1996
4.	Al2O3-YSZ	Step	100% YSZ to 100% Al_2 O_3 in a step of 20 v/o	24 GPa-13 GPa	Not Reported	P.Sarkar	1996
5.	WC-Co	Continuous	17 wt% Co- 4wt% Co	21 GPa- 9GPa	1290 C- 1340C	S.Put et al.	2001
6.	ZrO2-WC	Continuous	0% WC- 55wt% WC	900kg/mm2- 1800kg/mm2	1450C at 28 Mpa	S.Put et al.	2002
7.	WC-Co-Ti(C,N)	Continuous	Ti(C,N)—5wt%-0wt% Co---5-7wt% to 10-15wt%	20.5 GPa- 16.1GPa	1450 ^{0}C	S.Put et al.	2003
8.	Ce-TZP/Al2O3	Continuous	0wt%-60wt%	9 GPa-16 GPa	1600 C in air for 1 hrs	S.Put et al.	2003

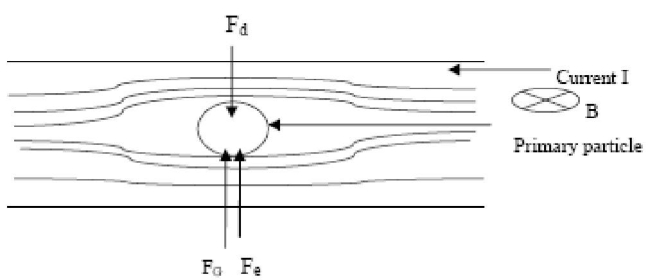

Figure 4 : Principle of Electromagnetic separation

2.2.3 Basic Principles of Electromagnetic Separation based FGM Manufacturing

The phenomenon of electromagnetic separation (EMS) with an application to manufacturing of materials was first discussed by Marty & Alemany[56]. However, the basic work in this area goes to the credit of Leenov & Collin[57] where they calculated the magnetohydrodynamic forces experienced by spherical particles. Zhennming and his co-workers[58] applied these concepts to produce an in-situ surface composite of Al-15wt% Si. The motion of melt and primary particles in an applied magnetic field can be visualized with the help of Figure 4. The mathematics of this approach is quite intricate however we present key mathematical equations so as to understand how this happens.

The electromagnetic Archimedes forces[59] as experienced by primary particles because of the difference in electrical conductivity between the parent melt and primary particle assuming the particles are spherical is:

$$\mathbf{Fe} = \frac{3}{2}\frac{\sigma_1 - \sigma_2}{2\sigma_1 + \sigma_2}\frac{\pi d^3}{6}|\mathbf{J}\times\mathbf{B}| \quad (2.1)$$

Parent melt is the material which primarily constitutes the material while primary particle are the inclusions whose material distribution we are interested in controlling using the above equation and equations presented ahead.

Similarly, the buoyant force experienced by such a primary particle is:

$$\mathbf{F_b}\ \textbf{(Buoyant Force)} = \left(\frac{\pi d^3}{6}\right)[\rho_2 - \rho_1]\,\mathbf{g} \quad (2.2)$$

Apart from this the drag force will be:

$$F_d = C_d\left(\frac{\pi d^2}{4}\right)\left(\frac{\rho_1 v^2}{2}\right) \quad (2.3)$$

Applying Force balance we arrive at what we call as terminal migration velocity (v_t) of primary particle in the melt.

$$(v_t)^2 = \left[\frac{3}{2}\frac{\sigma_1 - \sigma_2}{2\sigma_1 + \sigma_2}\left|J \times B\right| + g(\rho_2 - \rho_1)\right]\frac{4d}{3C_D\rho_1} \quad (2.4)$$

C.Song and his fellow researchers[60] have produced Al-22% Si-3.9% Ti-0.78% FGMs by this technique however issues like dependence of material distribution on melt solidification rate, initial alloy compositions and electromagnetic force was not discussed in detail however reasons behind three layer formation in their FGMs were cited. In continuation of this work the effect of above parameters on movement velocity, movement time and volume fraction distribution of inclusion within the FGMs was discussed in their next work in 2006 with a combination of Al-Mg-Si system[61]. They came out with the conclusion that there exists a critical value of electromagnetic force to be applied for in-situ formation of FGMs and below this value the resulting material distribution is homogenous and not graded. A summary of effect of various parameters on properties of FGMs is detailed ahead in TABLE 2.

TABLE 2 : Effect of process parameters of EMS on properties of FGMs

		Process Parameters of Electromagnetic Separation			
		Electromagnetic Force(EMF)	**Mould Preheating temperature**	**Pouring temperature**	**Initial Alloy composition**
Effect on properties of Primary particles when Process Parameters are increased in magnitude.	(1) Volume fraction of primary particles. (PVF)	Increases in lower part with increasing EMF's.	Increases with increase in mould preheating temperature.	No significant effect	Increases.
	(2) Particle free Region Length	Longer when EMF increases.	Increases with increase in mould preheating temperature.	No significant effect	Increases.
	(3) Particle size.	Decreases with increase.	Increases with increase in mould preheating temperature.	No significant effect.	Increases.
	(4) Volume fraction gradient.	Increases with increase.	Increases with increase in mould preheating temperature.	No significant effect.	Increases.

C.Song[62] while studying the electromagnetic separation of Al/Al_3 Ni FGMs came with few significant facts. They explored that why after certain range of primary particle content the particle volume fraction of FGMs decreases and reported that beyond a certain value it was not possible for particles to move to bottom part of FGM sample because of congestion and so even particles with large size also could not migrate to lower parts as predicted from above equations.

Apart from applying uniform magnetic field literature reveals synthesis of FGMs and composite materials using high and varying magnetic field as well[58,63,64]. X.Peng et al.[65] applied varying magnetic field for a combination of ZrO_2- Ni. This resulted into fabrication of ferromagnetic-nonmagnetic FGMs because of distinct difference between the susceptibilities of materials. FGMs combinations attempted using the potential of electromagnetic force are listed in TABLE 3.

TABLE 3 : Significant material combinations via EMS.

S. No	Material Combination of FGM	Author	Year of Fabrication	Nature of Gradient attained
1.	5 wt % Y_2O_3-AlN	T.S Suzuki et al.	2005	Continuous
2.	Al-Si-Ti	C.J Songa et al.	2005	Continuous
3.	Al-Mg_2Si-Si-Ti	C.J Songa et al.	2006	Continuous
4.	Mn-Sb	Tie liu et al.	2007	Continuous
5.	Al/Al_3Ni	C.J Songa et al.	2007	Continuous
6.	Al-Mg_2Si	C.J songa et al.	2007	Continuous

LASER ASSISTED MANUFACTURING OF FGMS

With increasing development the various laser assisted techniques are also used for synthesis of FGMs, however most of it has been done to improve the surface properties only. In this section the various Laser based technologies are visited comprehensively.

Laser cladding

The laser cladding is considered to be one of the most relevant technologies for preparing FGMs out of all laser assisted technologies. It is also known as one of the commercial hard facing method[66]. This technique can be classifies into two categories namely: (i) Pre-placed Powder Technique (ii) and Blown Powder technique. In former the powder is preplaced with a binder on substrate material to stick to it until the complete melting by laser takes place in an inert atmosphere while in later the powder is blown directly in to a laser generated melt pool[67]. In 1993 Jasim et al.[68] have produced Al-SiC FGMS using this technique along with laser alloying on a nickel alloy substrate and produced a functionally gradient region on the substrate by overlapping numerous laser processed tracks. Y.T Pei et al. 2000[69] have produced FGMs with a combination of Al/Si wherein the size as well as the volume fraction of Si particles enhanced from top to bottom of FGM. In an extension to this work Pei et al. 2001[70] have studied the five-fold twinning and growth features of Silicon particles. Riabikana et al.[71] produced functionally graded multilayer coating on M2 high speed tools steel of 34%, 50 % and 75% and found the maximum hardness value of 1600 HV which is quite above the working hardness of tool steel. Another significant work using this technique which is worth mentioning is of Jiang et al 2002[72]. They developed a Laser Based flexible fabrication process (LBFF) which was a computer integrated and numerically controlled however the base was laser Cladding. They used this technique for the production of functionally graded mould inserts[72]. Pintsuk et al. 2003have used laser sintering (Blown powder technique) for production of PFCs of tungsten and copper with main focus on W-25vol% Cu and W-60vol% Cu[73]. Laser Cladding is undoubtedly a good technique however various issue like sometimes bad wetting behaviour is usually noticed and also the sharp interlayer always exists. This is a potential cause of failure of materials produced by this technique.

Selective laser sintering (SLS)

SLS is basically a material accretion technology and produces the parts in a layer by layer fashion. This technique can be directly coupled to a CAD model and the powders used in this process are bound using a focussed energy source. It is recommended that an appropriate binding mechanism must be identified for binding contagious powders which ultimately result in the formation of green body[74]. The two well known binding mechanisms are melting and sintering. In the first consolidation approach, some sophisticated powder feed and control systems are required while as in the later, distinction of phase of material is needed. In the approach of sintering, the two established techniques are liquid phase sintering (LPS) and solid phase sintering (SPS). LPS is known to be a very fast technique[75]. This technique has been used up to good extent for FGM synthesis. LPS was used by Z.Z Fang for WC-Co graded composites with continuous gradient in cobalt content[76]. Functionally graded Nylon-11 composites filled with varying volume fractions of glass beads were prepared by Chung & Das[77] with an intention to improve the mechanical properties of polymers. They fabricated compliant gripper and rotator cuff scaffold and thus indicated that complex mechanical parts with improved mechanical properties can be manufactured using this technique.

Apart from these two prominent techniques covered in section 3.1 and 3.2 researchers have applied various other Laser assisted technologies for FGM preparation like selective laser melting[78], Laser Engineered Net Shaping[79-82], Laser rapid forming[83] etc. however these two techniques are dominant over others.

A VISIT TO OTHER TECHNOLOGIES OF FGM SYNTHESIS

The various other significant techniques which are employed by various researchers for FGM synthesis are discussed in this section. These techniques are unique in their functionality and have own advantages.

Spark plasma sintering (SPS)

This method is considered to be one of the advanced methods of sintering and is also known by other names like Pulse Electric Current Sintering (PECS). The unique capability of this method to manufacture highly compact materials in a small span of time at low temperatures makes it stand apart from other methods[84]. The significant aspect of this technique is a pulse of DC current is passed through the die in which the powder is stacked as well as the powder which is normally conductive. The Spark Plasma Sintering (SPS) process is based on the electrical spark discharge phenomenon: a high energy, low voltage spark pulse current momentarily generates spark plasma at high localized temperatures, from several to ten thousand between the particles resulting in optimum thermal and electrolytic diffusion. The detailed schematic representation of a SPS system is outlined in Figure 5.

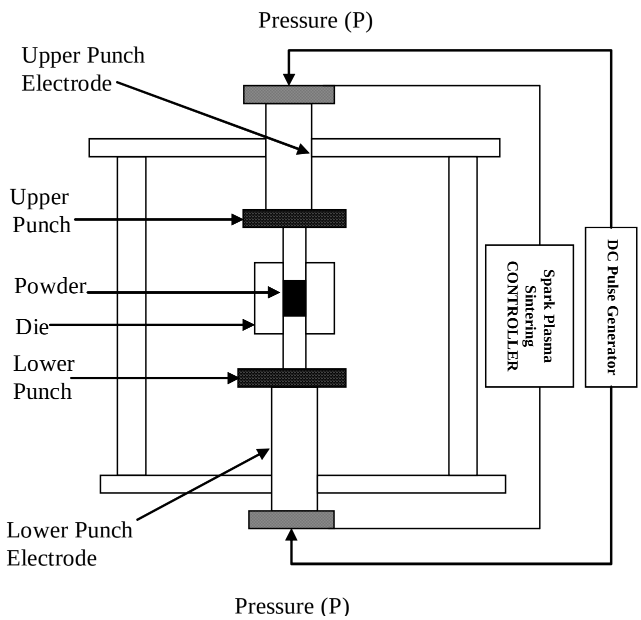

Figure 5 : Set up of spark plasma sintering machine.

The unique advantage of this technology is that it is capable of sintering like and dissimilar materials, seamless bonding, and material surface treatment. In addition, this technology does not require a green state, binders, or a pre-sintering stage; it is capable of producing net and near net shapes directly from powder. A comprehensive review of key factors like electric field and pressure on final material formed after synthesis and consolidation is given elsewhere[85]. Due to its vast capabilities numerous researchers have used this technique for producing defect free FGMs.

A novel combination of Al_2O_3 and Ti_3SiC_2 has been used for FGM preparation by L.Yongming et al.[86] to combine the properties of both. Ti_3SiC_2 exhibits both electrical as well as thermal conductivity while alumina is superior for its hardness, refractory property, chemical stability and insulation. It was observed in their work that the FGMs prepared showed electrical conductivity comparable to metals when the critical volume fraction of Ti_3SiC_2 was 30 wt%. SPS is also applied for preparing Bio-active FGMs for possible orthopaedic applications using HA/Y-TZP[87]. Six layered FGMs of a very important material combination of Ti-TiB_2-B was synthesized by H.Feng et al.[88], the idea was to combine the excellent property of TiB viz. extreme hardness, high melting point, good thermal shock resistance and chemical inertness keeping it on one side of FGM while on the other side the pure Ti was used.

Boron Carbide has been in the eyes of FGM community for a long because of its low density, chemical resistance and extreme hardness. Apart from these this material exhibits high neutron absorption characteristics which makes it suitable for nuclear applications as well however at high strain rates this shows suppressed fracture toughness. Hulbert and his fellow researchers have produced continuous FGMs using SPS for this material combination[89].

It is evident that SPS is superseding the traditional methods of sintering and is a potential time saver when the sintering is needed in a short duration thus increasing productivity.

Physical vapour deposition (PVD)/ chemical vapour deposition (CVD)

The two important vapour deposition techniques are PVD/CVD. These techniques are used for FGM coatings for long. However in due course of time there has been a constant improvement in these two techniques and numerous variants of these techniques have come up. We shall cover these techniques briefly.

Physical vapour deposition (PVD)

PVD is considered to be a promising technology for the formation of thermal barrier coating. The coatings produced by this method exhibits excellent thermal shock resistance, erosion resistance and do not require additional polishing[90]. The point which is worth mentioning about this technique is that the vaporization depends upon the vapour pressure of the material which is to be coated and so it becomes difficult to evaporate materials simultaneously which have large difference in their vapour pressure. The term PVD in itself is containing many important aspects. It engulfs in itself all those vacuum deposition process where the material to be coated is evaporated in vacuum condition and the vapour phase is allowed to form a coating on the substrate material however the utmost care should be taken that substrate material should be vacuum resistant[91]. A detailed description of a PVD apparatus is illustrated elsewhere[92]. Various variants of PVD like partially reactive physical vapour deposition, magnetron sputtering, resistance heating, high energy-ionized gas bombardment and electron-beam(EB) are available now a days and are extensively used for produced for functionally graded coatings on various substrate materials. EB-PVD has been successfully implemented to produce functionally graded coating of NiCOCrAlY on substrates of super alloys by Schulz[93]. Various coatings like Ti-CN[91], Cr_7Cr_3 and Cr on metals[94] are also reported. One worth quoting advantage of PVD is that it is suitable for components with close tolerance.

Despite of several advantages of this technique the various issues to be addressed are: its pertinent difficulty in producing efficient oxide coating, reduced stability of FGM coatings in high temperature environment and vacuum resistance.

Chemical vapour deposition (CVD)

The CVD can be explained as a process where a reactant gas mixture is allowed to pass through a high temperature reactor that consists of a glass tube normally in the range of 1-2 metre in length, to form a thin coating at the surface of the substrate. The normal temperature range is about 800^0C to 1200^0C. Functionally Graded coatings can be produced at slow to moderate deposition rate of about 5-10 pm /hour by just varying the ratio of source gas mixture or by controlling the deposition temperature, gas pressure or gas flow rate. K.L Choy in his exhaustive review of this process has elaborated principles, mechanism of deposition, reaction chemistry, kinetic phenomena and thermodynamics[95]. This technique has been used for FGM coatings of numerous combinations like SiC/C, Cr_3C/Ni, Ti/TiN, SiC/TiC, ZrC/C, BN/Si_3N_4 on C/C Composites . CVD coating are also preferred in cases where high abrasion resistance is needed. CVD is undoubtedly a very old technique for producing FGM coating but has many demerits like requirement of high deposition temperatures, production of environmentally unacceptable chemical wastes and slow deposition rate. A comparison of both the techniques PVD/CVD is presented in TABLE 4.

TABLE 4 : A comparison of PVD & CVD

Parameters	Deposition Rate & atmosphere	Deposition temperature range	Oxide Coating Formation	Waste By product	Structure of Coating & Thickness Range	Various Variants of PVD/CVD	Type of Process
PVD	Faster and performed in vacuum	100-600 C^0	Difficult	Environmentally Acceptable	Crystalline as well as amorphous; 2-5 μm	Thermal Evaporation, EB-PVD, Magnetron sputtering, Ion plating, ion.	Line-of Sight process.
CVD	Slow to Moderate and performed in controlled atmosphere	800-1200 C^0	Can be produced	Environmentally Unacceptable.	Crystalline as well as amorphous; 6-10 μm.	Low Pressure CVD, plasma Enhanced, photochemical, aerosol assisted & Laser CVD	Non-Line of sight Process

Combustion synthesis

Combustion synthesis is a technique which has been used by researchers to fabricate FGMs since inception of FGM concept. Numerous combinations of various materials for preparing FGMs have been used by various researchers.

Combustion synthesis is a technique which heavily depends upon the exothermic reactions which are self-sustaining and are energy wise efficient. In combustion synthesis reaction the reactant powders are mixed in a definite stoichiometric proportion and pressed into a pellet of a specified green density and then ignited. The ignition can be performed either locally at one point or by heating the whole pellet up to the required ignition temperature of exothermic reaction. There are various reported strategies for initiating reaction like radiant flux, laser radiation, resistance heating coils, spark and chemical ovens etc. Burkes et al.[96] describes combustion synthesis as a method with operating simplicity, rapid cooling rates and short reaction times that permit control over Ostwald ripening and ease of production equipment containment.

There are two modes for combustion synthesis reaction: (i) Self propagating Mode (ii) & Simultaneous combustion mode. In the Self Propagating Mode the combustion is initiated at one point in the reactant sample and this spreads throughout the reactant mixture in the form of combustion wave and propagates throughout. The simultaneous combustion mode is just contrary to it and the reaction takes place simultaneously throughout the reaction mixture as soon as the sample attains the ignition temperature and is generally conducted in a furnace.

The various advantages of combustion synthesis are:

(i) Capability to volatilize low-boiling point impurities and because of generation of high reaction temperature resulting in high quality products.
(ii) The expensive processing is not required.
(iii) Low operating and processing cost.
(iv) The synthesis and consolidation of inorganic materials in one step is possible.
(v) SHS can also be applied for producing thin coatings and films on substrate materials with improved bonding between the two.

The various significant combination combinations which have been attempted by researchers are NiTi-TiC_x, Ti-B, TiC-Ni, $MoSi_2/Al_2O_3$, TiC-NiAl etc.

Impeller dry blending (IDB)

The credit of first reported study regarding IDB goes to A.J Ruys[97] and his fellow researchers at Centre for Advanced Materials Technology at Sydney University Australia. This method claims to offer the possibility of producing large bulk FGMs with an easy control of continuous gradient and compositions. The whole manufacturing strategy of Impeller dry blending can be summarised in four steps namely: feeding, Blending, Homogenisation and Deposition.

The feeding is initiated by two separate feed hoppers for two component powders. The second step involves careful blending of two powders using control gates such that it starts with 100% volume ratio of first powder and zero % of second powder. The blending ratio is then varied in a controlled way as the feeding of powders continues. The third step is the homogenisation of the blended powder mix using an impeller chamber and finally the deposition takes place. The two unique features of IDB which sets it apart from other techniques of FGM preparation are controlled segregation and controlled blending. The biggest advantage of this technique is that processing times are less and has capability to produce large bulk FGMs with continuous gradients.

As addressed previously the issue of creating a continuous gradient is still a primary problem of importance while attempting to produce large bulk FGMs. IDB method claims to produce gradient which is either linear or at the least mathematically regular[97]. The second problem is of densification as when going for ceramic-metal FGM there usually lays difference in melting point temperature of metal and ceramic and in turn the choice of sintering temperature is a typical issue. This issue is solved by use of hydrostatic shock forming where a focussed explosive charge transmits a shockwave through conical water column into the blend which generates localized pressures more than 30 GPa.

CONCLUSIONS

In the area of functionally graded materials a basic paper which can expose beginners does not exist in literature. As the area of FGM is still evolving, hence the need was felt to write a comprehensive review which can summarise all significant work in this area. In this work the focus has been to present various manufacturing strategies of FGMs in a simple and lucid manner with an intention to encourage various young researchers to the area of functionally gradient materials. A new classification is proposed which overrides previous classification of FGM preparation techniques. Effort is done to cover all important fundamentals of significant manufacturing techniques. All important material combinations which have been used by various researchers throughout the globe using different techniques with reference to application area are also covered in this work. A comprehensive tabulation is made for gradient information and material combinations for various techniques covered in this work wherever necessary. The intention of authors has been to discuss the challenges associated with the area and illustrating the merits and demerits of manufacturing strategies for functionally gradient materials.

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