

Analysis of Synthetic Methods to Create Functionally Gradient Materials

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I. INTRODUCTION

For many engineering applications, a material which has mechanical and chemical properties which are different throughout the solid is desired. Coating or joining were the traditional methods for accomplishing this, but the interface between the materials is prone to failure due to magnified stress and incomplete joining [1]. The ideal solution is a material which gradually changes its structure toward the surface, transitioning from one pure material on the inside to a different pure material on the outside. This type of material is called a functionally gradient (or graded) material, abbreviated FGM. Creating FGMs is a new field, and most procedures are material specific and require significant modifications to utilize with different materials.

The aerospace industry has experimented with several metal-ceramic FGMs to use as strong, heat-resistant shells for spacecraft [2]. Biomedical research has also been significant, with metal-bio-active FGMs for use in bone replacement surgeries [3]. These FGMs are superior to other materials, and allow the possibility of long-lived spacecraft in the former, and speedy, nearly perfect recovery for patients on the other. The applications of FGMs are currently limited to well-funded fields like these because of the high cost of design and synthesis. If a more universally applicable and inexpensive synthesis were devised, almost all coated materials could be replaced by structurally superior FGMs. This would significantly lessen the current limitations on engineering projects, opening up new design possibilities in applications from ovens (with much smaller housings and better insulation) to corrosion-free bridges.

II. PRINCIPLE/MECHANISM OF SYNTHESIS

Several methods of synthesizing FGMs have been researched. The most common method involves powder metallurgy (PM), where fine powders of materials are combined into a green product which is then sintered. The combining of the powders, particle size, mixture ratios, and heating methods all differ between applications. The principles behind each of these steps will be analyzed here in detail. Other synthesis methods which will be discussed are combustion synthesis and laser melt injection (or cladding).

Mixtures

To determine the proper mixture of starting materials, several approaches can be taken, with the choice depending on the nature of the materials and the extent of information available about them. For mixtures of well-known materials, phase diagrams may be used to determine stable gradients. Figure 1 shows the phase diagram of a Si-Al-O-N system which was used to determine which mixtures could be used to merge Si_3N_4 - Al_2O_3 [4]. The six phases between β and AlN seen in the phase diagram were excellent candidates for gradient layers, as they were naturally stable mixtures. When stable mixtures are not known to naturally occur, trials with different mixtures may be created for the PM method using:

$$C=(x/d)^p \quad (1)$$

where C is volume fraction of one component, x is the distance of the FGM layer from the surface of the material, d is the thickness of the FGM layer, and p is the compositional distribution factor of the component. The value of p is changed with each trial, and the theoretical density is determined using Equation 1. When the experimental density matches the theoretical density, the ideal mixture has been found [5].

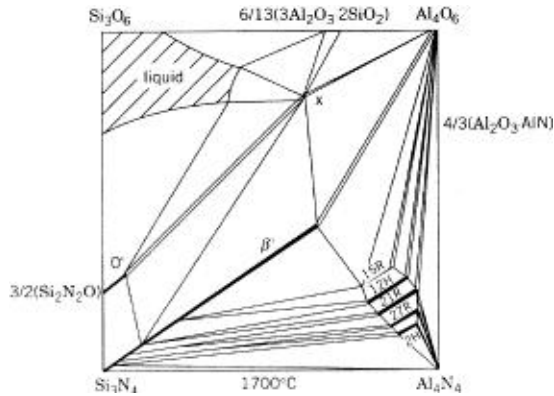


Fig. 1. The Si-Al-O-N system (1700°C)

Numerous computer simulation programs have recently been devised to design FGMs, but little research has been done using them as yet [6]. Various numerical methods to optimize certain properties by changing volume ratios have also been proposed, with most becoming exceedingly complicated very quickly [7]. The simplest numerical method is the "Voigt-type mixture rule", which optimizes one property for a binary mixture

$$P = f_A P_A + f_B P_B \quad (2)$$

where P is the property, A and B are the components, and f is the mole fraction of each component [4]. The others will not be discussed further here, as most of the actual syntheses are based on trial and error, not complicated equations. However, if the synthesis of FGMs is ever to be perfected, these methods must be improved first to allow better predictability and understanding.

Combining and Layering in PM and Combustion Syntheses

Once the proper mixtures have been determined, the powdered materials are stacked or layered in a metal die (usually steel). The simplest method for layering is to just lay the first mixture in the die, then the next, then the next, and tap the die to settle the powders. This

method has not had good results, however, as differing particle sizes between components can create an overabundance of the smaller component on the bottom and the larger on the top [8]. To prevent intermixing of layers, different mixtures are often milled with alcohol and then dried and sieved to create evenly sized pre-mixed composite powders. These milled powders are then layered in a die, and as all particles are essentially the same size, the layers remain distinct [2]. The thickness of the layers may be determined using an alternate form of Equation 1. To doubly ensure the layers don't migrate, low-pressure pre-compacting may be performed on each layer [9]. Once all the layers have been added to the die, the material is usually cold-pressed into a compact green body [4]. Preliminary tests on the material can be conducted at this point, including density measurements, dimensions, and micrographs [8].

Sintering

In the PM method, the green bodies are sintered below the melting points of the component materials. Sintering is the process by which small particles coalesce to form larger particles, initiated by heat and driven by surface area reduction [10]. The smaller the particles the greater the driving force for the reaction, which is why fine powders are used in powder metallurgy. The mass transfer in sintering occurs by liquid or solid phase diffusion or vapor phase transport. Because the "neck" between two touching spheres is concave, the activity in the neck is lower than elsewhere on the surface, and material migrates from high activity to low activity [11]. Figure 2 shows a representation of how the particles coalesce in the sintering process [12]. As the necks fill in, the four spheres eventually become one.

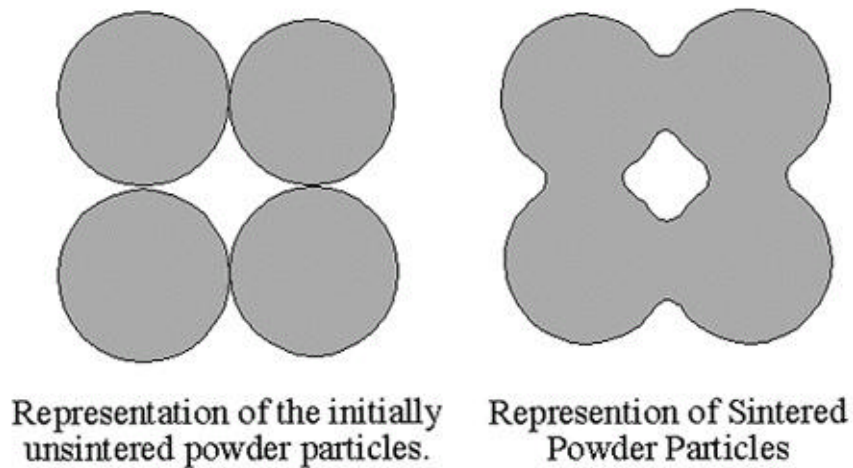


Figure 2. Sintering

The heat which triggers the sintering process may come from several different sources. Traditionally, a furnace is used for powder metallurgy, and the temperature and duration of heating are determined experimentally [5]. More recently, more uniform grain sizes have been obtained using microwave ovens to sinter the green body [3], with the temperature and duration again being experimentally determined. Occasionally, sintering is accomplished by hot pressing, where pressure is applied with the heat [2] in order to assist the sintering process.

Laser Melt Injection

Unlike powder metallurgy, laser melt injection (LMI) combines the components of the FGM in liquid state. LMI is specifically designed for FGMs which are pure material through most of the bulk and have gradual introduction of another material out to one surface [13]. The surface of the substrate is melted with a laser as a stream of powdered material is added to the melt behind the laser. The velocity and positioning of the laser beam determines how

deep and to what extent the added particles penetrate the substrate, and the nozzle which delivers the powder produces homogeneous spreading of the powder at each depth. A schematic representation of an LMI apparatus is shown in Figure 3 [14]. The gray area in this figure represents the melt and the white arrows show the paths the particles take into the substrate. By carefully planning the angles of delivery and melting, a functionally graded layer can be added to the substrate. The extent of grain growth is not controlled in this method, as the temperature is kept above the melting point for the entire injection process [14].

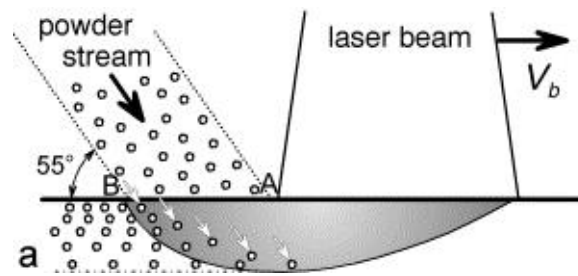


Figure 3. Sketch of the laser particle injection process.

Combustion Synthesis

One drawback of the synthetic methods described above is the energy that must be put into them. Heating a furnace or firing a laser beam is expensive, and maybe unnecessary if the formation of the FGM is an exothermic reaction. Combustion synthesis requires only an initial input of energy to begin the reaction, which then generates its own heat and self-propagates. Once the combustion has started, a very hot (up to 4000 °C) combustion front travels through the material very quickly. The heat released by the combustion melts the materials and allows speedy recrystallization and reorganization. The mechanism of all phases of combustion is not understood in great detail, and each application requires a

lengthy research period to determine what explosive gases may evolve and what unexpected constituents may appear [15]. The starting material for combustion synthesis of FGMs is a green body formed as described above. Instead of sintering, as in PM, the green body may be briefly heated to expel gases, and then ignited. Research has shown that it is necessary to ignite the less exothermic constituent first to avoid explosion, and allow the combustion front to reach its highest temperature only at the end. This is easily accomplished in a binary system which grades between a pure, slightly exothermic component and a pure, highly exothermic component [16].

III. APPLICATION

The results of selected experiments involving the synthesis methods described produced generally favorable results. Most researchers conducted tests on their products to determine the microstructure and strength of the FGMs, and these results will be compared here. In general, the combustion synthesis is the most economical and effective method for a limited number of applications, while the powder metallurgy method is less affordable but highly effective for more varied applications.

Application of PM

The experiments which used milling, cold pre-compacting of the green body and then sintering with pressure yielded well-joined and distributed FGMs. Figure 4 shows the micrograph of the product from such an experiment using SiC/Cu, a ceramic-metallic FGM. No obvious voids or separation between layers is observed, and the strength tests did not show significant weakening near the interfaces [5]. Figure 5 shows the micrograph of a ceramic composite FGM which was made this way and designed to be more machinable.

Their results were actually better than expected, and the applications for ceramics which can be easily cut without sacrificing too many beneficial properties are very exciting [2].

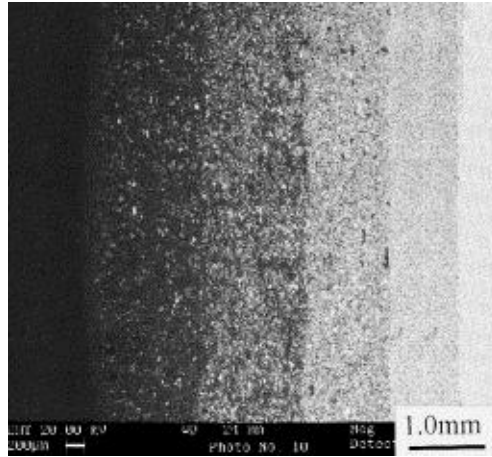


Figure 4. SEM of overall six-layered SiC/Cu FGM with $p=1.0$ (Cu contents are 0, 20, 40, 60, 80, 100 vol.%, respectively).

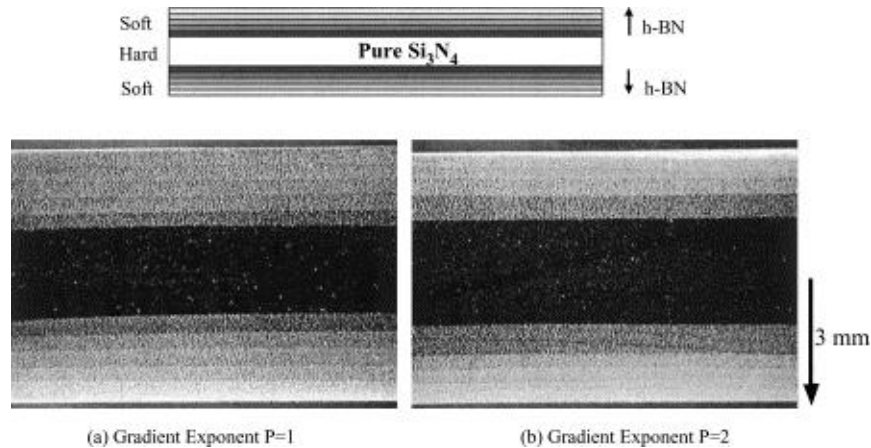


Figure 5. Schematic illustration and sintered specimens of machinable Si₃N₄/h-BN FGMs.

The results of the PM experiment without milling were very different from these. All but one sample broke during sintering, and that last one fractured along an interface at the first stress. This experiment was very useful to show that milling and sieving are necessary (but costly) steps in the PM process [8].

Application of LMI

The applications of LMI are much more limited than other syntheses because the grain growth is not controlled or completed. When surface strength is more important than other properties, this method is not a good option. However, it does maximize chemical properties, such as corrosion-resistance. Figures 6 [14] and 7 [13] are the micrographs of products obtained by LMI, showing the lack of uniform gradient which intensifies stress. Also notable is the lack of vacancies or undesired products, which optimize chemical properties. Strength tests were not conducted, as this method is known to reduce strength, but conductivity tests were as expected.

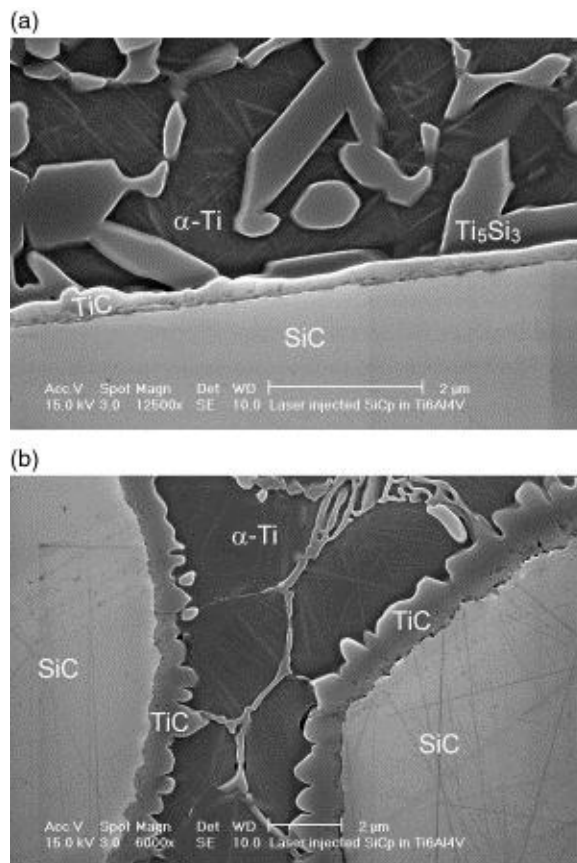


Figure 6. SEM micrographs showing: (a) monocrystalline TiC reaction layer formed at a flat facet of SiCp; and (b) cellular polycrystalline TiC layer surrounding SiCp.

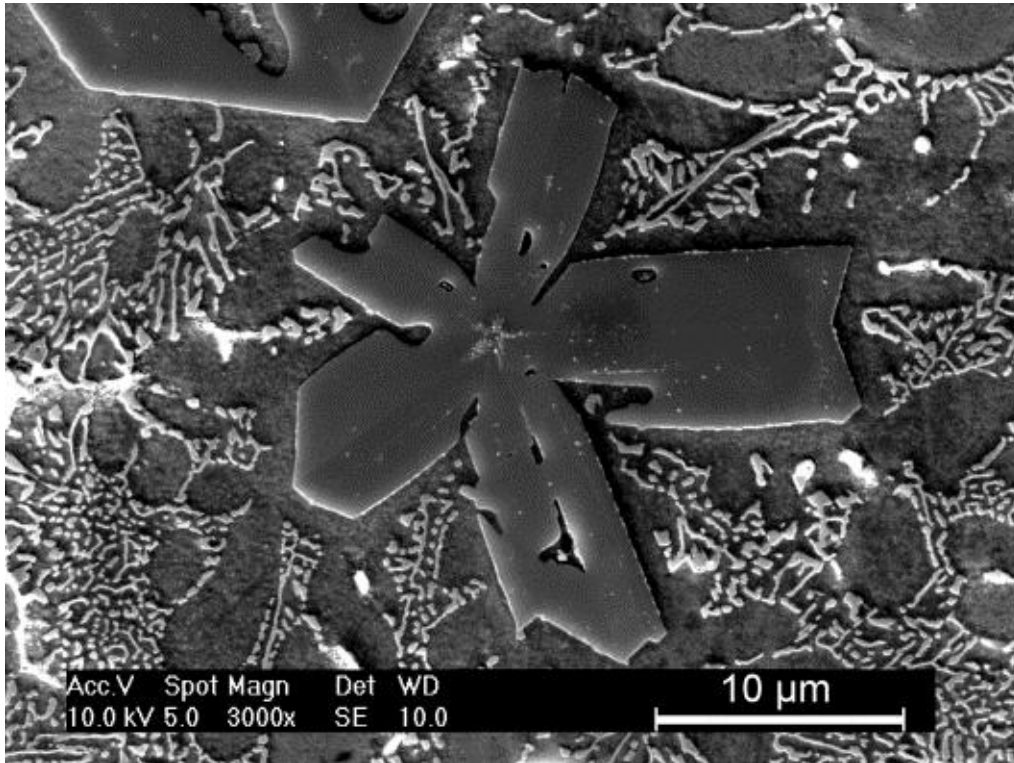


Figure 7. SEM micrograph showing the growth feature of the five-branch Si particle and the surrounding α -Al dendritic halos as well as the eutectic adjacent to α -Al.

Application of Combustion Synthesis

The selected combustion synthesis was completely successful, once the gases had been expelled and the less exothermic material was ignited first. The product was structurally sound and evenly graded as planned. No significant changes in shape or failures were detected in the product, and the interfaces were strong. Figure 8 shows the micrograph of the product, a ceramic-metallic FGM, illustrating the smooth gradient and lack of voids or defects [16].



Figure 8. Cross-section of a five-layered FGM after combustion synthesis reaction.

IV. CONCLUSION

The synthesis of FGMs is an important research field, as no one method has yet been perfected for all the desired FGMs. Three major methods of synthesis were considered in this paper, namely, powder metallurgy, laser melt injection, and combustion. Powder metallurgy has broad applications, but is not cost-effective due to all the steps and instruments required for successful synthesis. Experiments conducted to try to reduce the number of steps required have not succeeded, so PM may never be a truly affordable synthesis route. Laser melt injection is a good substitute for coating when only chemical properties are being considered, as it does not form a homogeneously graded structure. It is not an acceptable choice for stressed applications, and does not have the wide applicability that PM does, although it is less time-consuming. Combustion synthesis is cost-effective and does produce chemically and physically sound products, but it is poorly understood. Until the mechanisms of combustion are known in better detail, each application must be more extensively researched than with other methods. With continued research, synthesis of FGMs will improve, and affordable functionally graded materials will be in common use in all aspects of our lives.

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