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Functionally graded electrical/thermal ceramic systems

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Abstract

Ceramic–metal and ceramic–ceramic functionally graded materials (FGMs) show promise for hypothesised applications such as thermoelectric converters, graded solid oxide fuel cells, graded piezoelectrics, electrically insulating joints, heatsinks for fusion reactors, and thermal barrier skins for lightweight spaceplanes. Most research has focussed either on FGM films (microns across), or modelling of hypothetical FGMs. Large bulk-FGMs with continuous (not layered) gradients are ideal for the above listed applications, however existing bulk-FGM powder-processing technologies give little gradient control and slow processing throughputs. The authors have developed a new process, impeller-dry-blending, which offers the possibility of producing large bulk-FGMs of a wide range of controllable continuous gradients and compositions. In this, the first published study of the impeller-dry-blending process, Cu–SiC and stainless steel–SiC FGMs were fabricated. Electron microscopy and elemental analysis revealed linear compositional gradients across cross sections of several millimetres. Densification was by vacuum sintering and hydrostatic shock forming. © 2001 Elsevier Science Ltd.

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1. Introduction

Functionally graded materials (FGMs) are two component composites characterised by a compositional gradient from one component to the other. Ceramic–metal and ceramic–ceramic FGMs show great promise as specialised electrical materials, and thermal barrier materials. Ceramic–metal FGMs are an ideal solution to the problem of metal–ceramic bonding. Hypothetical applications for FGMs currently being considered throughout the world include: thermoelectric converters, graded solid oxide fuel cells, graded lead zirconate titanate, electrically insulating joints (metal surface–ceramic core), high heat flux sinks for fusion reactors, and thermal barrier skins for lightweight spaceplanes.

Traditional composites are homogeneous mixtures and therefore involve a compromise between the desirable properties of the component materials. In contrast, an FGM is a two-component composite characterised by a compositional gradient. Since significant proportions of an FGM can contain the pure form of each component, the need for compromise is eliminated and the properties of both components can be fully utilised. Thus, for example, the toughness of a metal can be mated with the refractoriness of a ceramic without compromising the toughness of the metal side or the refractoriness of the ceramic side. FGMs are also ideal for minimising thermomechanical mismatch when bonding dissimilar materials.

The three broad categories of FGMs are: FGM films, interface-FGMs and bulk-FGMs.[1] FGM films are thin graded coatings (10^{-6}–10^{-4} m thick) which provide an ideal solution to the problem of film-substrate thermomechanical mismatch. They have been intensively researched since the early 1990s. Interface-FGMs (10^{-4} m–10^{-3} m thick) are films that are used to bond two dissimilar materials. They are the FGM category closest to full commercial exploitation. FGM films and interface-FGMs are well-developed technologies.

By contrast with these thinner materials, bulk-FGMs have large graded cross-sections (10^{-2}–10^{-1} m thick) and a large volume of each component phase. They possess great potential where operating conditions are severe, such as extreme electrical or thermal barriers, and also

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have potential in some novel applications such as graded solid oxide fuel cells and graded lead zirconate titanate.

The technologies to create a continuous gradient in FGM films are well established. Yet the manufacture of bulk-FGMs still presents significant problems. For example, 16 years on from the now famous 1984 Japanese FGM space plane premise that precipitated the global interest in FGMs, space shuttle hulls are still clad with bonded ceramic tiles. FGM hulls are still a hypothesis.

To date, almost all bulk-FGM research has focussed on the computer modelling of theoretical properties rather than the measurement of actual properties of manufactured bulk-FGMs.[2] This is largely because it is difficult to manufacture regularly-graded bulk-FGMs using the current forming methods of layering and segregation.

Layering proceeds by sequential slip casting,[3] sequential thixotropic casting,[4] sequential extrusion,[5] or a dry powder metallurgy approach. The layering method is inadequate because it produces an FGM with a number of sharp interfaces between each layer. Continuous grading is preferable in terms of thermomechanical stress distributions

Controlled segregation uses gravity to segregate the two component powders on the basis of their true density. This approach has been the focus of most researchers, and includes sedimentation forming, slip casting, centrifugal casting, thixotropic casting, and infiltration of graded pore structures.[6] It is very difficult to achieve regular reproducible gradients this way because of dependence on particle size, size distribution, particle interaction, slurry rheology, true density, and so on. This approach does not produce a readily predictable or controllable gradient profile.

The above listed methods are not ideal for producing a bulk-FGM that is commercially viable because they do not provide a regular continuous gradient, that is, one which is linear or at least mathematically regular, whereas the best thermomechanical stress tolerance arises from a graded region that is broad, continuous and regular. Moreover, these methods are problematic for mass production.

An answer may be the innovative extension of controlled component blending from the manufacture of FGM Films to the manufacture of bulk-FGMs as proposed by this study. In this method, the two FGM components are blended to produce a mathematically-regular gradient. This offers the advantage of producing precisely controllable regular functional gradients independent of the powder density and gravitational settling of the components (the features which vitiate the segregation approach). Controlled blending techniques used so far to manufacture *FGM films* include thermal spraying (blended powder feed),[7] vapour deposition (CVD/PVD blended gas feed),[8] electrophoretic deposition (blended slurries),[9] filter pressing (blended slurries),[10] and blended spray drying.[11] These techniques are not used to fabricate bulk-FGMs.

This study has involved the development of an innovative controlled blending process: impeller-dry-blending, described in the method section below. The impeller-dry-blending process, recently developed by the authors, is a rapid large-throughput process that overcomes the key problem of a continuous compositional gradient: dependence on differences in true density and particle characteristics of the two FGM components. It is therefore ideal for commercialisation of bulk-FGM manufacture.

A second problem with bulk-FGMs is densification. In the case of ceramic-metal FGMs, the melting point, and therefore the sintering temperature, of the ceramic is generally very much higher than that of the metal. For example:

- aluminium (660°C)–alumina (2050°C)
- copper (1080°C)–magnesia (2800°C)
- stainless steel (1400°C)–silicon carbide (2700°C)

Combustion synthesis was originally proposed as a solution to this problem in Japan at the inception of the FGM concept in the mid 1980s. However, this limits FGM manufacture to the rare situation where the components are combustible. In the majority of commercially viable or useful metal–ceramic and ceramic–ceramic combinations, this is not the case.

Hot pressing enables sintering to take place a few hundred degrees below that required for pressureless sintering. However, with the melting point differentials of typical metal-ceramic combinations commonly in excess of 500°C, this is usually not viable either.

Our proposed solution to this densification problem is hydrostatic shock forming. A focussed explosive charge transmits a shockwave through a conical water column into the FGM powder blend. The use of a focussed explosive charge enables localised pressures in excess of 30,000 MPa to be achieved, i.e. 30 GPa+, which is three orders of magnitude greater than the pressures for hot pressing, and in fact greater than the microhardness of ceramics (typically 10–20 GPa). Therefore, at such pressures, ceramics can flow hydrodynamically. This, coupled with instantaneous adiabatic heating from the detonation, gives the potential for good densification of metal–ceramic or ceramic–ceramic FGMs with grossly different melting points between the two components. Explosive forming is a well-established metal-forming process, and we believe that it will ultimately prove to be amenable to adaptation to FGM densification.

2. Experimental procedure

The impeller-dry-blending process involves four stages, through which the powders pass, in sequence:

- Feeding: feeding of the two component powders from two separate feed-hoppers.
- Blending: metering of the ratios of the two powder streams using control gates such that (vol.% component 1) + (vol.% component 2) = 100% at all times.
- Homogenisation: homogenisation of the blended powder mix using an impeller chamber.
- Deposition: the homogenised blend deposits like "snowflakes" into a mold beneath the impeller chamber.

The feeding and blending stages are subjected to vibration, so as to enhance flow. The process begins with the blend ratio (100% powder 1) and (0% powder 2). The blend ratio is then varied in a controlled way as powder flow continues, and the process ends when the settings are (0% powder 1) and (100% powder 2). Typically, powder 1 is a metal and powder 2 is a ceramic. The impeller-dry-blending process is the subject of a provisional patent application.

We have investigated a number of powder combinations, including copper–stainless steel, bronze–stainless steel, alumina–aluminium, alumina–titanium, silicon carbide–copper, and silicon carbide-stainless steel. While the list of FGM possibilities is endless, we have focussed most of our efforts on the silicon carbide-stainless steel and the silicon carbide–copper FGM systems, and these form the basis of the present study. We used the following powders:

- Stainless steel powder — 316L grade, Sintec, Australia.
- Copper powder — Sigma Aldrich, Australia.
- Silicon carbide powder — a standard abrasive grade from Norton, Australia.

Hydrostatic shock forming trials involved the use of PE4 plastic explosive (ADI Australia) with a detonation velocity of ~8 km/s. The FGM specimens were deposited into cylindrical mold cavities 25 mm in diameter. After deposition, they were either cold-pressed at 100 MPa, and then vacuum sintered at 1300°C, or hydrostatic-shock-formed inside a three-piece mild steel containment system comprising: *top piece* — explosive charge canister; *middle piece* — steel disk with a central cone containing water for hydrostatic shock transfer; *lower piece* — steel disk containing the FGM in a central 25 mm diameter cylindrical mold cavity that mated with the water-filled cone in the middle piece.

After densification, the specimens were sectioned longitudinally, polished, and then assessed for gradient profile using scanning electron microscopy and elemental analysis by energy dispersive spectroscopy. The elemental analysis was conducted over a 4 mm wide, 4 mm long region of the specimen straddling the entire 4 mm long graded zone. Elemental analysis involved a series of axial (perpendicular to the direction of the gradient) line scans, each spanning the entire 4 mm width of the area of interest. Each successive line scan was 200 μ further along the graded zone. The average intensity of iron and silicon for each line scan was then plotted as a function of the position along the graded zone, and thus a data point (position, intensity) was plotted at each 200 μ increment across the gradient.

3. Results and discussion

The impeller-dry-blending process proved to be very rapid and efficient. Optimal throughput rates were in the order of 1 cm of gradient buildup per minute. Most experiments were conducted using a 25 mm cylindrical mold. For larger molds, larger hopper orifices were required for the same throughput rate. Thus the impeller-dry-blending process fulfilled the expectation of being a rapid low-cost high-throughput process for fabricating large bulk FGMs.

Fig. 1 shows the compositional profile of a vacuum sintered stainless steel–silicon carbide FGM, across the 4 mm long graded region. The regression fit of the data is superimposed. The correlation coefficient was 0.96 for the iron, representing a close approximation to linearity. The correlation coefficient was only 0.83 for the silicon, indicating a significant deviation from linearity. This was most likely indicative of the fact that silicon, being a light metal, is much more difficult to detect with precision by semi-quantitative energy dispersive spectroscopic methods.

Therefore, while the data suggest a good approximation to linearity on the gradient of both the metal component (stainless steel, represented by iron), and the ceramic component (silicon carbide, represented by silicon), the semi-quantitative nature of elemental analysis

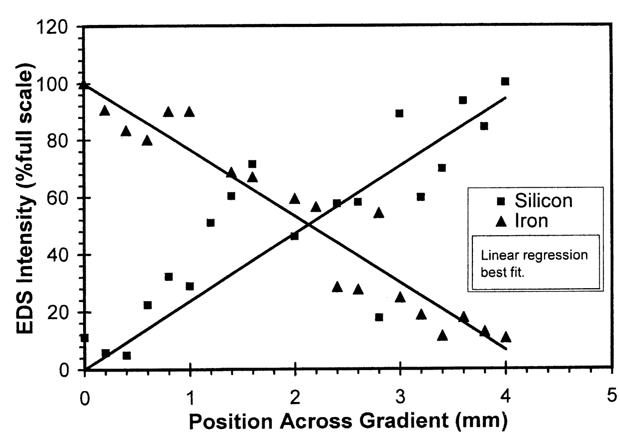

Fig. 1. Elemental analysis plot of the iron (stainless steel) and silicon (silicon carbide) concentrations across a 4 mm graded region of a stainless steel–silicon carbide FGM.

by energy dispersive spectroscopy limits the precision of this study. Future work will focus on elemental mapping using electron microprobe microanalysis with more precise light element detection capabilities. Preliminary trials have commenced on this approach, and much system optimisation in terms of specimen preparation and probe parameters will be required before electron microprobe microanalysis can yield a more precise outcome than the current energy dispersive spectroscopy line-scan approach.

A series of electron micrographs across the graded region are shown in Fig. 2. These, when viewed in sequence, convey qualitatively the evenness of the gradient. Therefore, the results in Figs. 1 and 2 suggest that the impeller-dry-blending process has given a linear continuous gradient, which can be considered to be a successful outcome for this first preliminary study of the impeller-dry-blending process. A linear continuous gradient is a significant improvement over the layered gradients produced by previously reported layering methods, or the sharp irregular gradients of previously reported segregation methods.

The micrographs also reveal significant porosity in the structure. This is a result of the fact that these specimens were vacuum sintered, and the sintering temperature of the stainless steel is much lower than that of the silicon carbide, with the result that the FGM was only partially sintered and suitable only for characterisation by microscopy and elemental analysis, not for mechanical testing. Preliminary investigations into the solution to this problem, hydrostatic-shock-forming, showed some promise.

The hydrostatic-shock-forming trials are in an early stage of development. We have thus far conducted our first hydrostatic-shock-forming trial on the copper–silicon carbide FGM system. The results of this trial were encouraging. We succeeded in densifiying the silicon carbide by this process. The microhardness of silicon carbide is ~27 GPa, and would therefore require a pressure wave >30 GPa for hydrodynamic flow. The resultant densified microstructure suggests that our calculated prediction of 30 GPa+ was probably achieved, thereby enabling the densification of the silicon carbide by shock-wave induced hydrodynamic flow. The micrographs in Fig. 3 show a small amount of porosity and an unusual interconnectivity of the pores. This seems to be indicative of the fact that the material flowed during densification. Some cracks can be seen, which may have arisen from insufficient densification, inhomogeneity of the pressure wave, or localised stresses. Work is ongoing

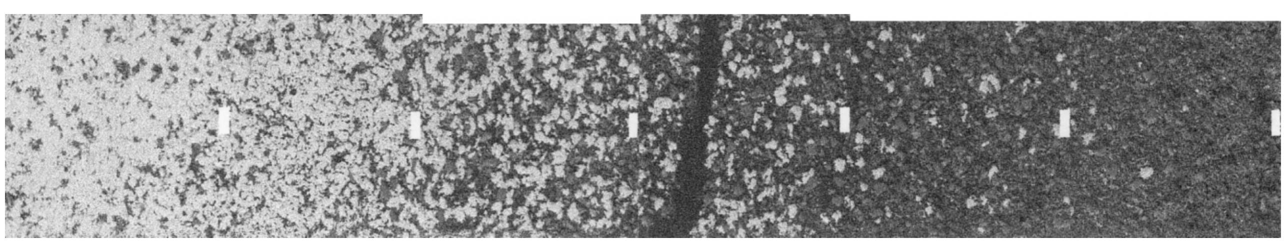

Fig. 2. Six electron micrographs of adjacent regions across the graded region of the FGM analysed in Fig. 1. From the stainless steel rich end (a) through to the silicon carbide-rich end (f). Note the stress crack in image (d), probably due to thermal contraction during sintering. Bar = 100 μ.

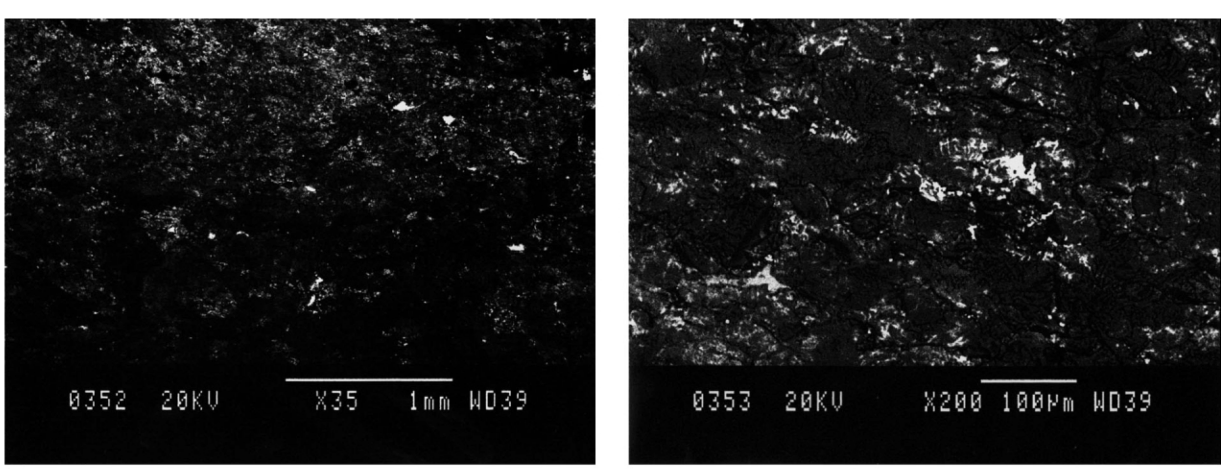

Fig. 3. Electron micrograph of the polished surface of the silicon carbide region of a hydrostatic-shock-formed SiC–Cu FGM. Note the small amount of porosity and the unusual interconnectivity of the pores in (b), perhaps indicative that the material flowed during densification.

in this regard in terms of understanding the dynamics of the hydrostatic-shock-forming process. The bonding of the copper was insufficient due to excessive hydrodynamic flow of the copper, and thus elemental analysis measurements of the gradient were not possible.

Future hydrostatic-shock-forming trials will involve revised containment systems to minimise stress inhomogeneities, the use of presintered specimens (instead of green specimens), and a reduced explosive charge quantum to attempt to optimise the hydrodynamic flow to enable densification of the ceramic without excessive flow of the metal.

4. Conclusions

This is the first study published on our impeller-dry-blending process. The focus of this paper was on establishing the general suitability of the impeller-dry-blending process for bulk-FGM manufacture. This work also points to future developments in terms of precise gradient quantification by electron microprobe elemental mapping, and enhanced densification strategies via hydrostatic-shock-forming. In general, this study yielded four key conclusions:

1. This study has demonstrated the viability of the impeller-dry-blending process for producing linear-gradient continuous bulk FGMs.
2. Impeller-dry-blending processing times were in the order of 1 cm/min, i.e. very rapid.
3. Hydrostatic-shock-forming trials are in the early stages, but the process shows promise.
4. The stainless steel–silicon carbide and copper–silicon carbide FGM systems of this study are merely representative of the potential of this impeller-dry-blending/hydrostatic-shock-forming approach. There are many electrical/thermal ceramic FGM systems with commercial applicability that can be investigated in future studies.

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