

Application of poly(methylsilane) and Nicalon[®] polycarbosilane precursors as binders for metal/ceramic powders in preparation of functionally graded materials

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For the first time, ceramic precursors were applied in the powder metallurgy (P/M) preparation of Functionally Graded Materials (FGM). Two types of FGMs were prepared: Al/SiC for possible aerospace applications and Cu/SiC for dynamic seal applications. There are two main advantages of using ceramic precursors for P/M preparation of FGMs (1) avoidance of the commercially used debinding step and (2) shrinkage control of the individual layers of the composite.

1. Introduction

The concept of functionally graded materials (FGMs) was proposed [1,2] in the last decade as a means of preparing thermal barrier materials suitable for use in aeronautics (hypersonic aircraft skins), fusion reactors, and space transportation systems. An FGM is an anisotropic composite material in which a continuous change in microstructure from low modulus (usually metal) to high modulus (usually ceramic) domains result in a gradation of properties. An abrupt transition in material composition from pure ceramic to pure metal, due to the low coefficient of thermal expansion of the ceramic and relatively high thermal expansion coefficient of the metal, [3,4] results in severe thermal stress which encourages the propagation of interfacial cracks. A well-controlled interlayer may relieve stress acting across the bonded interface and may thus prevent crack formation. This technique is especially applicable within materials which exhibit thermal-expansion mismatch.

Depending on the application of the FGM, the gradient can be created in a single step, in a continuous or in a stepwise fashion. The single step gradient is comprised of a uniform mixture of metal and ceramic sandwiched between pure ceramic and metal layers. In a continuous gradient the mixtures of metal/ceramic blends gradually vary from ceramic-rich to metal-rich layers. The stepwise gradients are achieved by steps in composition of ceramic-rich to metal-rich layers (Fig. 1).

The interest in the field of FGMs is constantly growing [5–7]. The application of FGMs can be found wherever corrosion, wear, and heat-blocking are required such as in the fuselage of a hypersonic aircraft which, due to aerodynamic heating, may experience temperatures of up to 1700 °C [5, 6]. Ceramic

tails, traditionally used for this purpose, tend to debond at the metal–ceramic interface as a result of thermal stress. Other applications of FGMs also may be found in biotechnology for bone implants, eg, a Ti/hydroxyapatite FGM [8].

The FGM preparation methods include: various powder metallurgy (P/M) techniques, [9] plasma spray techniques, [10,11] chemical vapour deposition, [12] self-propagating high temperature synthesis (SHS), [13–16] as well as magnetron sputtering, physical vapour deposition, dynamic ion mixing, chemical vapour infiltration, and reaction bonding [17]. Powder metallurgy processes, due to their speed, simplicity, and economy, are employed mostly for FGMs that are composed of layers (plies) with a thickness in the order of millimeters. The powder techniques generally are divided into dry and wet processes.

An FGM is prepared by dry powder metallurgy in a number of ways. In one of these, dry powders such as Al, Si, and ZrO₂ [18] or SiC, C, ZrO₂, and TiC [19] are deposited successively by thermal spraying and subsequently compacted by cold isostatic pressing (CIP) prior to sintering. Another dry P/M process of FGM preparation consists of sintering of a powder compact at high temperature (1500 °C) at a high isostatic pressing (HIP) of 12.5 MPa [20].

In wet P/M most of the powder processes require binders. For example, an injection molded Fe-Co alloy/stainless steel (SUS 304) FGM required 7–11 wt% of an organic binder (such as poly(vinyl acetate) or polyethylene) which had to be removed in vacuum at 350 °C prior to sintering [21]. Another process for the preparation of functionally graded materials utilizes a suspension of metal and ceramic powders in water and is analogous to the packing of

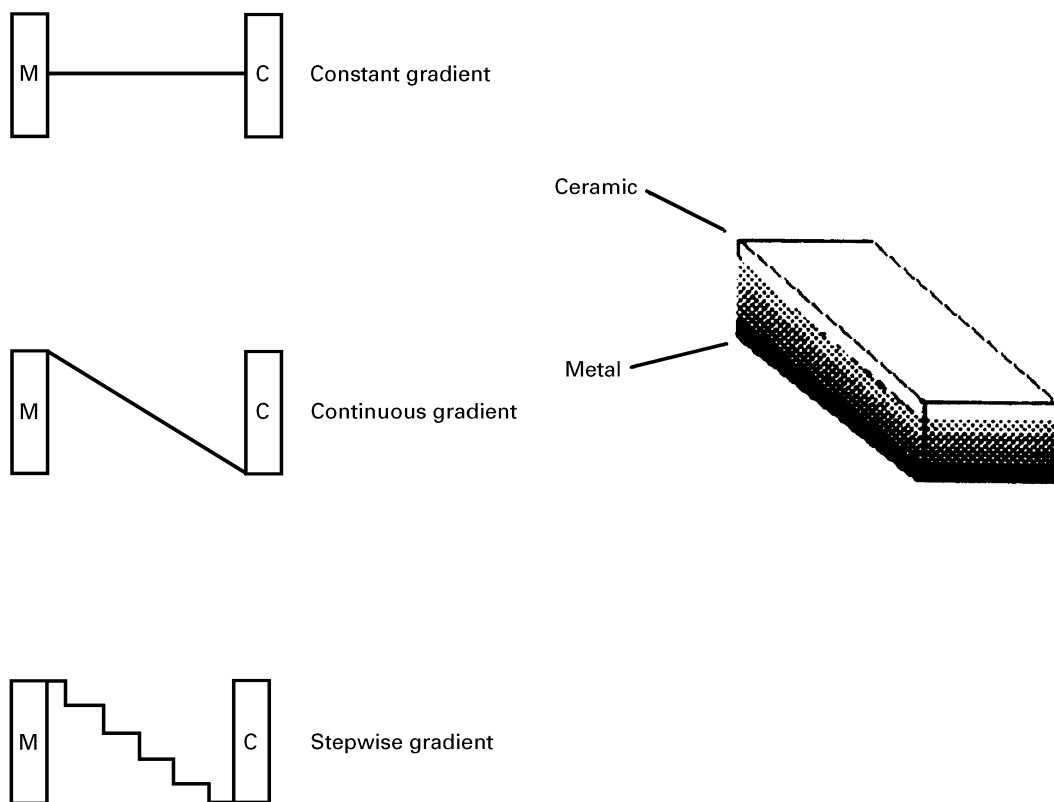


Figure 1 Functionally Graded Material (FGM); M-metal, C-ceramic. After Suganuma *et al.* [1].

a liquid chromatography column. The gradual variation in suspension composition from metal-rich to ceramic-rich gives the gradient. In the final step, solid/liquid separation is carried out and the resulting cake is dried at 100 °C in vacuum [22].

Yoshitaka *et al* [5] and Takemura *et al* [6] have extensively explored the thin sheet laminating process which involves the preparation of a slurry and the subsequent use of a doctor blade technique for preparation of thin sheets. These sheets may vary in thickness from tens of microns to about 2 mm. They then are overlaid and uniaxially pressed in a way to give the final composition gradient. The green laminate preform requires a debinding (dewaxing) step prior to sintering which involves heating the green FGM to 500 °C with an air pressure of 0.5 MPa.

In both wet and dry P/M, the shrinkage of the laminate layers may cause deformation in the final product. The shrinkage control of individual layers of the FGM composite is important, especially when powders of various particle sizes are used. If shrinkage is not addressed, total warpage of the FGM composite takes place. It is essential to make all the layers of the laminate shrink equally during sintering to avoid deformations of the final part. Niino and coworkers in reference [17] showed that when 0.03 μm particle size ZrO₂ is blended with Ni (~4 μm) powder, the percent shrinkage increases with an increase in volume fraction of ZrO₂; however, the reverse is the case when 15 μm particles of ZrO₂ are employed. It also was observed that the volume shrinkage ratio was nearly equal to the volume fraction of organic binder in the green body. Therefore, successfully controlled shrink-

age requires the incorporation of a mixture of different sized ZrO₂ particles in conventional P/M preparation of FGMs. In general, the shrinkage of parts prepared from powders depends on powder characteristics such as size, shape, and size distribution [23].

In the preparation of FGMs by powder metallurgy, to date only organic binders have been utilized; there is no precedent in the literature of using preceramic polymers as binders for the fabrication of FGMs. Recently, it has been shown that preceramic polymers serve excellently as binders for ceramic powders in the fabrication of shaped ceramic parts [24–26]. When the part is sintered, pyrolysis of the preceramic polymer occurs with minimal evolution of gases to give a high yield of ceramic residue, which is retained in the part [27]. Preceramic polymers may be used as binders for metal powders for the *in situ* fabrication of metal matrix composites (MMCs) [28,29]. In both cases, the utilization of a preceramic polymer does not require the debinding step and the preceramic polymer also acts as an *in situ* source of ceramics. The ceramic phases formed in this process are derived from the reaction of the metal and the ceramic precursor yielding, in most cases, metal carbides and silicides.

We report here an improved powder metallurgy technique for FGM preparation which involves the use of preceramic polymers as binders for metal/ceramic powder blends and provides shrinkage control of each individual layer. The preliminary results of this technique as applied to two thermal-expansion mismatched systems, Cu/SiC and Al/SiC FGMs, are described [30].

2. Experimental procedure

2.1. General comments

All green powder preparations of metal and polymeric ceramic precursors were conducted in an air-free atmosphere using standard Schlenk line and dry-box techniques. Toluene was distilled from sodium under an Ar flow. Metal powders were purchased from Cerac and were handled in the dry-box at all times: Al (cat. # A-1182; lot # X14720) and Cu (cat. # C-1133; lot # X14557). SiC powders were obtained from: Cerac ($< \mu\text{m}$); cat. # S-2022; lot # X15459) and City Chemical Corp. NY, 600 mesh.

Nicalon[®] polycarbosilane (PCS) was purchased from Dow Corning Corp., X9-6348, lot# PG 110064. Ceramic precursors were prepared using published procedures: PCS crosslinked with $\text{Co}_2(\text{CO})_8$ and PMS. The particle size distribution of Al, Cu, and SiC (all from Cerac) is shown on Fig. 2.

2.2. Preparation of Cu/SiC FGM by using powder Cu substrate

The following powder mixes were prepared (Tables I and II):

The dry mixes were suspended in toluene and ultrasonic activation was used to maintain dispersion and the cleanliness of the surface of the metal powder. After overnight sonication, the solvent was removed under vacuum. The resulting powder was dried, pulverized in an agate mortar and pestle and passed through a 270 mesh sieve to assure a uniform particle size distribution. The powders then were compacted in a manner shown on Fig. 3. The layers were compressed uniaxially in a die at 43.1 MPa for 1 h. The green FGM compact was ejected from the die

TABLE I (constant amount of polymeric precursors)

| Mix No. | PCS ^a /SiC ($< \mu\text{m}$)/Cu molar ratio | Nicalon [®] PCS Precursor wt (g) | SiC ($< 1 \mu\text{m}$) weight (g) | Cu (– 325 mesh) weight (g) |
|---------|--|---|--------------------------------------|----------------------------|
| 1 | 0:0:100 | pure Cu powder | | |
| 2 | 5:0:95 | 0.96 | 0 | 20.00 |
| 3 | 10:0:90 | 2.03 | 0 | 20.00 |
| 4 | 10:10:80 | 1.00 | 0.69 | 8.76 |
| 5 | 10:20:70 | 1.00 | 1.38 | 7.66 |
| 6 | 10:50:40 | 1.50 | 5.20 | 6.60 |
| 7 | 10:90:0 | 0.87 | 6.00 | 0 |

^a Based on Si

TABLE II (gradual increase of polymeric precursor from Cu to SiC)

| Mix. No. | PCS ^a /SiC (1 $< \mu\text{m}$)/Cu molar ratio | Nicalon [®] PCS ^b weight (g) | SiC ($< 1 \mu\text{m}$) weight (g) | Cu (– 325 mesh) weight (g) |
|----------|---|--|--------------------------------------|----------------------------|
| 1 | 0:0:100 | pure Cu powder | | |
| 2 | 8:20:72 | 0.08 | 0.14 | 0.80 |
| 3 | 14:36:50 | 0.16 | 0.28 | 0.60 |
| 4 | 19:52:29 | 0.24 | 0.42 | 0.40 |
| 5 | 24:62:14 | 0.32 | 0.56 | 0.20 |
| 6 | 31:69:0 | 0.40 | 0.60 | 0 |

^a Based on Si

^b Crosslinked with $\text{Co}_2(\text{CO})_8$ [35]

and isostatically pressed at 275.8 MPa for 10 min and subsequently was fired in the furnace in argon at rate of 5°C min^{-1} to 250°C with a 2 h hold and 5°C min^{-1} to 900°C with a 3 h hold at that temperature. The entire pyrolysis was conducted under a uniaxial load of 200 g.

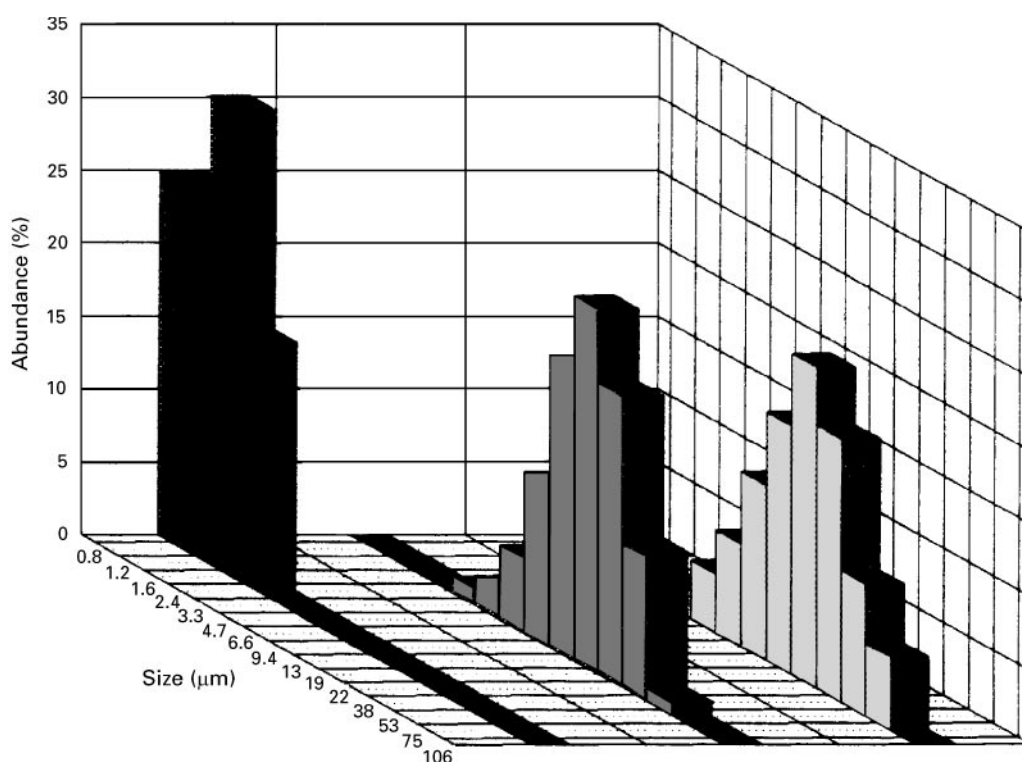


Figure 2 Particle size distribution of, (□) Al, (■) Cu, (■) SiC powders used for FGM preparation.

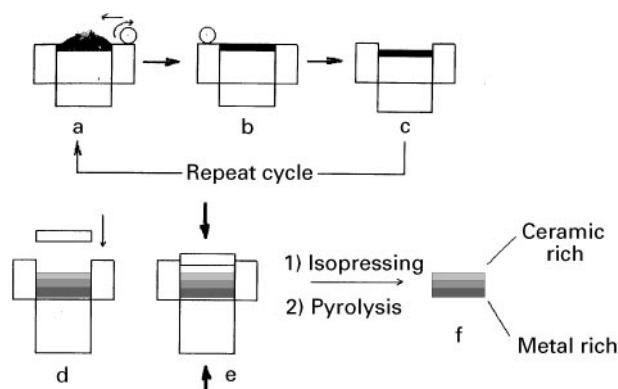


Figure 3 The process of FGM preparation using ceramic precursors as binders. (a) - deposition of green powder; (b) - smoothing of the powder bed by counter rotating the roller; (c) - lowering the powder bed for the next green powder composition; (d) - introducing the top punch; (e) - uniaxial pressing; (f) - the final product - FGM.

2.3. Preparation of Cu/SiC FGM by using a solid Cu substrate

The following powder mixes were prepared (Table III):

The mixes were prepared as described in the first experiment. The powders were deposited (in sequence: No.1, No. 2) on a solid (OFC) Cu plate ($1.25 \times 3.78 \times 0.15$ cm), the surface of which had been previously oxidized by extensive (15 min) polishing of the substrate on 4000 grit SiC paper in air using water as a coolant. The pressing and pyrolysis were conducted as described in the first experiment.

2.4. Preparation of Al/SiC FGM by using a powder Al substrate

The following powder mixes were prepared (Table IV):

The preparation and compaction of mixes were performed as described in the first experiment. The pyrolysis was effected at 5°C min^{-1} with a 2 h hold at 250°C , further pyrolysis at 5°C min^{-1} with a 3 h hold

at 550°C . The final pyrolysis took place at 1000°C for 3 h, at which temperature no outward signs of melting were observed.

2.5. Shrinkage experiment using cross-linked PCS precursor and SiC filler

Blends of PCS crosslinked with 1.0 mol% $\text{Co}_2(\text{CO})_8$ were prepared as depicted in Table V. The powders were suspended in toluene and ultrasonicated overnight. After removal of volatiles, the powders were pulverized in a mortar and pestle and uniaxially compacted at 620.7 MPa for 1 h and isostatically pressed at 275.8 MPa for 10 min. Green bodies were pyrolyzed at 5°C min^{-1} to 250°C with a 2 h hold and subsequently at the same rate to 1500°C with a 3 h hold at that temperature. The volumes and weights of the compacts before and after the pyrolysis are given in Table V.

3. Results and Discussion

Two FGM systems; Cu/SiC and Al/SiC, were prepared using polymeric ceramic precursors as binders. The Al/SiC FGM is of interest for possible aerospace application because of its light weight and high durability. The Cu/SiC FGM, on the other hand, may find its use in dynamic seal applications, as in mechanical face seals where corrosion resistance and good heat transfer ability are required [31].

The P/M FGM preparation process using pre-ceramic binders is much simpler than the conventional P/M techniques (Fig. 3). A 100-ml round-bottomed flask is charged with 2–3 cm^3 of the metal powder (generally – 325 mesh; the same powder used commercially in P/M) and various amounts of the polymer (based on silicon when an organosilicon polymer is used) and 30 ml of anhydrous solvent. The resulting suspension of the metal powder in the solution of the polymer is placed in an ultrasonic bath for 20–24 h. The sonic activation is necessary to clean the

TABLE III Cu/PCS/SiC powder mixes for the solid Cu substrate

| Mix No. | PCS ^a /SiC/Cu molar ratio | Nicalon [®] PCS weight (g) | SiC (– 600 mesh) weight (g) | Cu (– 325 mesh) weight (g) |
|---------|--------------------------------------|-------------------------------------|-----------------------------|----------------------------|
| 1 | 10:0:90 | 2.03 | 0 | 20.0 |
| 2 | 10:90:0 | 0.87 | 6.0 SiC; 0.12 B [32] | 0 |

^aBased on Si

TABLE IV Al/PMS/SiC powder mixes

| Mix No. | PMS ^a /SiC/Al molar ratio | PMS [34] weight (g) | SiC (< 1 μm) weight (g) | Al (– 325 mesh) powder weight (g) |
|---------|--------------------------------------|---------------------|-------------------------------------|-----------------------------------|
| 1 | 0:0:100 | pure Al powder | | |
| 2 | 10:0:90 | 1.10 | 0 | 6.07 |
| 3 | 10:10:80 | 0.92 | 0.84 | 4.52 |
| 4 | 10:20:70 | 0.71 | 1.30 | 3.05 |
| 5 | 10:50:40 | 0.50 | 2.28 | 1.23 |
| 6 | 10:90:0 | 0.87 (PCS) | 6.0 | 0 |

^a Based on Si

TABLE V PCS/SiC mixes used for shrinkage experiment (Fig. 10).

| Mix No. | PCS/SiC wt ratio | PCS weight (g) | SiC weight (g) | (I) Green body weight (g) (II) volume ^a (cm ³) | (I) Ceramic body weight (g) (II) volume ^b (cm ³) |
|---------|------------------|----------------|----------------|--|--|
| 1 | 0 | 0 | 2.86 | (I) 2.86 (II) 1.00 | (I) 2.81 (II) 1.00 |
| 2 | 2:8 | 0.4 | 1.6 | (I) 1.8415 (II) 0.83 | (I) 1.7235 (II) 0.60 |
| 3 | 4:6 | 0.8 | 1.2 | (I) 1.6590 (II) 0.91 | (I) 1.4606 (II) 0.60 |
| 4 | 6:4 | 1.2 | 0.8 | (I) 1.4064 (II) 0.94 | (I) 1.1785 (II) 0.50 |
| 5 | 10:0 | 1.1 | 0 | (I) 1.1000 (II) 1.04 | (I) 0.8565 (II) 0.35 |

^a Volume measured with a calliper

^b Archimedes volume, measured by displacement of isopropanol
 % shrinkage = (green volume - final volume) / (green volume)

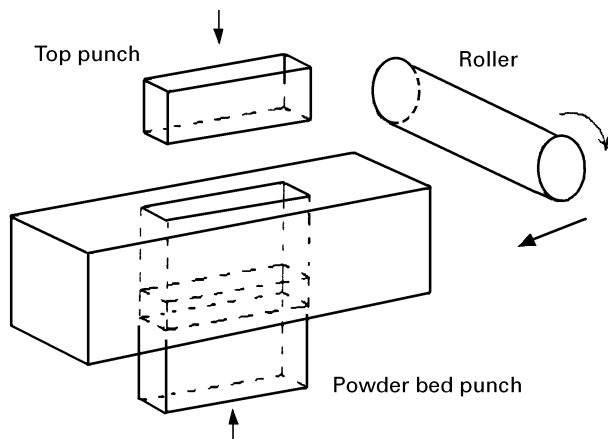


Figure 4 Schematic of a rectangular die used for FGM preparation.

surface of the metal particles and to ensure their homogeneous dispersion. Subsequently, the volatiles are removed at reduced pressure on a high-vacuum line with vigorous agitation. The solid residue is dried *in vacuo* at 50 °C overnight and ground to a fine powder using an agate mortar and pestle or a ball mill (for larger quantities). The pulverized green powder then is shifted through a 270 mesh sieve to remove large agglomerates. In some cases, in addition to metal powder and preceramic binder, a ceramic filler such as SiC is used for ceramic-rich plies. Once the powder premix has been prepared, the FGM preparation process involves a sequential formation of two-dimensional powder layers of varying metal/ceramic ratios containing constant or varying amounts of preceramic polymeric binder to yield a three dimensional FGM structure as depicted in Fig. 3. Each layer begins with a thin distribution of powder spread over the surface of the power bed. A retractable punch that supports the powder bed is then lowered so that the next powder layer may be introduced (Fig. 4). This layer-by-layer process is repeated until the final ceramic/polymer layer is applied (Fig. 3). Uniaxial and isostatic pressing then follow. Finally, the heat treatment/sintering (not involving debinding) is administered.

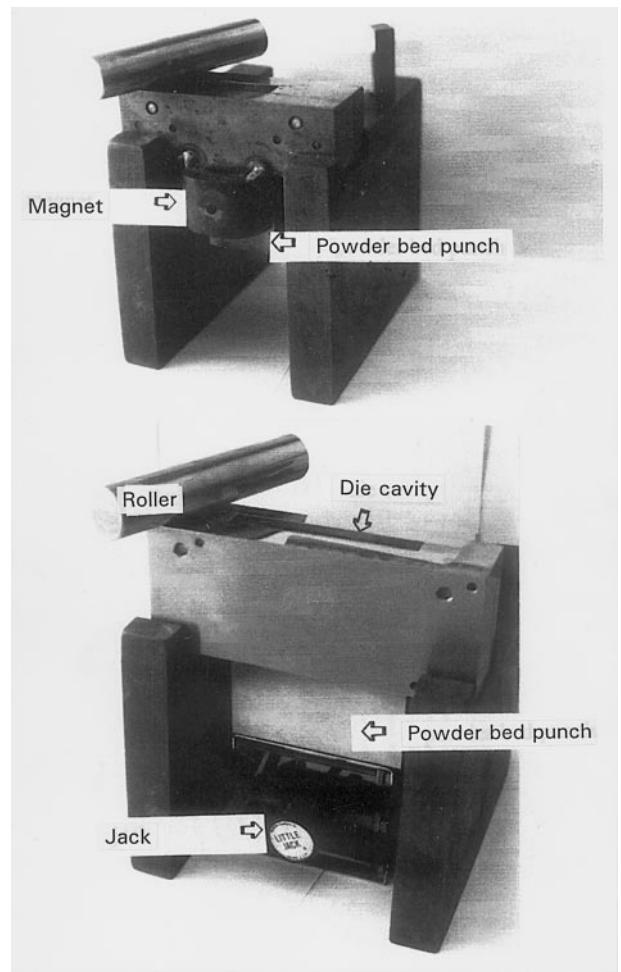


Figure 5 Rectangular dies for FGM preparation; a) powder bed punch supported with a magnet, b) powder bed punch supported with a jack.

The thickness of the FGM plies is controlled by the position of the powder bed punch. Two kinds of supports were used for the powder bed punch (Fig. 4). One support was made of a magnet permanently welded to the die which kept the ferromagnetic punch from sliding out of the die cavity (Fig. 5a). This setting is especially useful for overlaying nonmagnetic powders. The other support consisted of an adjustable jack placed under the powder bed punch (Fig. 5b).

Two types of Cu/SiC FGM have been prepared, one having a Cu powder substrate and the other having a solid 1/8" oxygen free copper (OFC) grade Cu piece. In both cases, a commercially available polycarbosilane (PCS) (the precursor to Nicalon® fibres) was used as binder, a source of ceramic, and as sintering agent for the SiC filler [32] (due to presence of excess carbon after the pyrolysis). Some of the crystalline phases generated in the Cu-FGM pyrolysis were SiC and $\text{Cu}_{0.83}\text{Si}_{0.17}$ is identified by X-ray powder diffraction [29].

When the Cu/SiC FGM is built up from a solid Cu metal base, the first powder layer comprises -325 mesh Cu metal powder and PCS while the last one contains the SiC powder and the PCS binder. The layers are compacted as shown in Fig. 3. Uniaxial pressing, isostatic pressing and heat treatment then follow. The solid Cu base requires a mild surface oxidation of the Cu surface to promote sintering of the Cu/PCS powder premix [33]. The surface oxidation was accomplished by extensive polishing of the substrate on 4000 grit SiC paper in air using water as a coolant. In both cases the pyrolysis at 900 °C with a 3 h hold at that temperature in Ar was conducted under a constant uniaxial 200 g load to prevent any deformation.

Fig. 6(a, b) depicts the cross-sectional area of the Cu/Si FGM made from the Cu powder substrate and 6 other layers gradually changing in composition from Cu-rich to SiC-rich (Table VI). It appears that good adhesion was achieved between all of the layers (Fig. 6b). The first two plies after the pure Cu layer were composed of Cu powder mixed with a PCS binder in the absence SiC filler in 95:5 and 9:1 mol ratio, respectively. All subsequent plies contained SiC filler.

Fig. 7a shows a cross-section of solid Cu coated with SiC having an intermediate layer (single step gradient) of Cu and PCS in a 9:1 molar ratio. The intermediate layer appears to be well sintered to the solid Cu plate. Fig. 7b depicts a bird's eye view of the Cu plate which has a very well bonded SiC patch (withstands attempted removal with a sharp object and a scotch tape test). Direct deposition of SiC/PCS in a 9:1 molar ratio powder on solid Cu also was accomplished (Fig. 7c). However, gradientless deposition of SiC yields a much weaker coat than the one with even a single step gradient. It appears that Cu from the solid substrate partly infiltrates the SiC face creating a self-generated gradient (Fig. 7c).

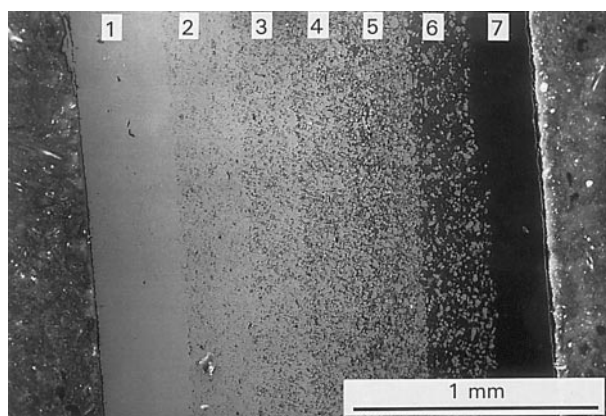


Figure 6a SEM micrograph of a cross-sectional area of Cu/SiC FGM prepared using powder substrates and SiC particle size of < 1 μm. The mix numbers correspond to Table VI.

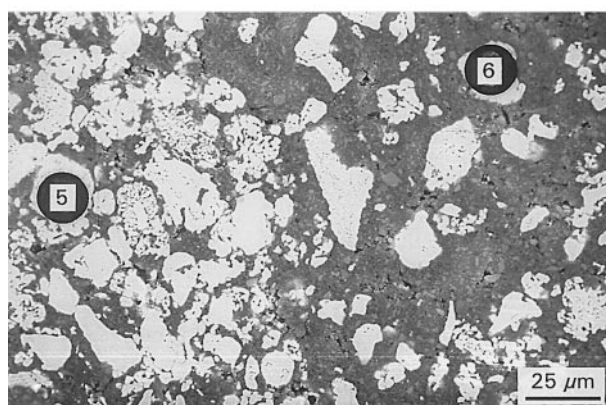
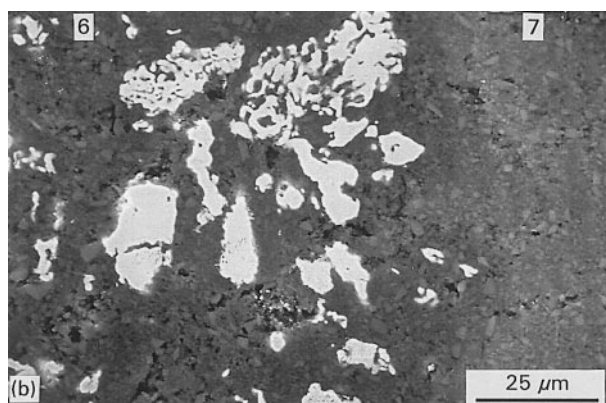


Figure 6b (2 parts) SEM micrographs of a two ply interface from the FGM in Fig. 6a). The mix numbers correspond to Table VI.

An Al/SiC FGM was prepared using Al powder, poly (methylsilane) (PMS) crosslinked with $(\text{Cp}_2\text{ZrH}_2)_n$, [34] and SiC as filler (Table VIII). Its pyrolysis in Ar at 550 °C with a 2 h hold at that temperature followed

TABLE VI Cu/PCS/SiC powder mixes with constant PCS content

| Mix No. | PCS ^a /SiC (< μm) /Cu molar ratio | Nicalon® PCS Precursor wt % | SiC (< μm) wt % | Cu (- 325 mesh) wt % |
|---------|--|-----------------------------|-----------------|----------------------|
| 1 | 0:0:100 | pure Cu powder | | |
| 2 | 5:0:95 | 4.6 | 0 | 95.4 |
| 3 | 10:0:90 | 9.2 | 0 | 90.8 |
| 4 | 10:10:80 | 9.6 | 6.6 | 83.8 |
| 5 | 10:20:70 | 10.0 | 13.7 | 76.3 |
| 6 | 10:50:40 | 11.3 | 39.1 | 49.6 |
| 7 | 10:90:0 | 12.7 | 87.3 | 0 |

^a Based on Si

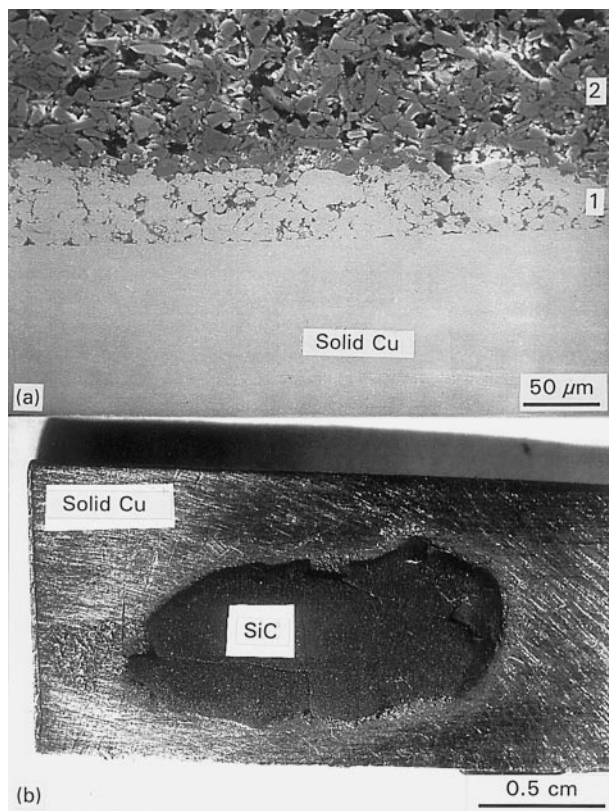


Figure 7 SEM micrograph of a cross-sectional area of Cu/SiC FGM prepared from the solid substrate and - 600 mesh SiC: a) having a single step gradient; b) bird's eye view of a bulk composite in a). The mix numbers correspond to Table VII.

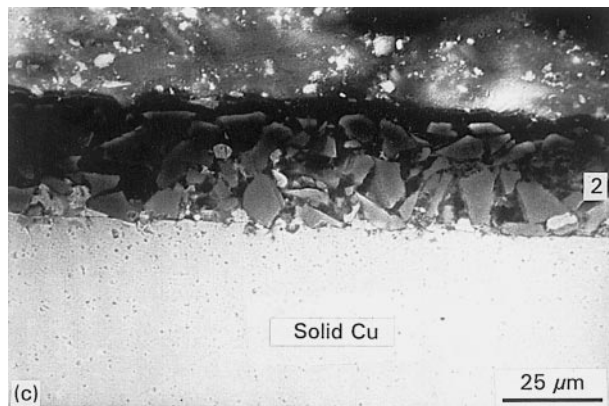


Figure 7c SEM micrograph of a cross-sectional area of Cu/SiC FGM prepared from the solid substrate and - 600 mesh SiC: c) directly deposited SiC/PCS powder onto Cu solid substrate. The mix numbers correspond to Table VII.

(Fig. 8a) by pyrolysis at 1000 °C with a 3 h hold yielded a composite with retained bulk structural integrity. Fig. 8b depicts the cross-sectional area of the four laminate composite material pyrolyzed in Ar at

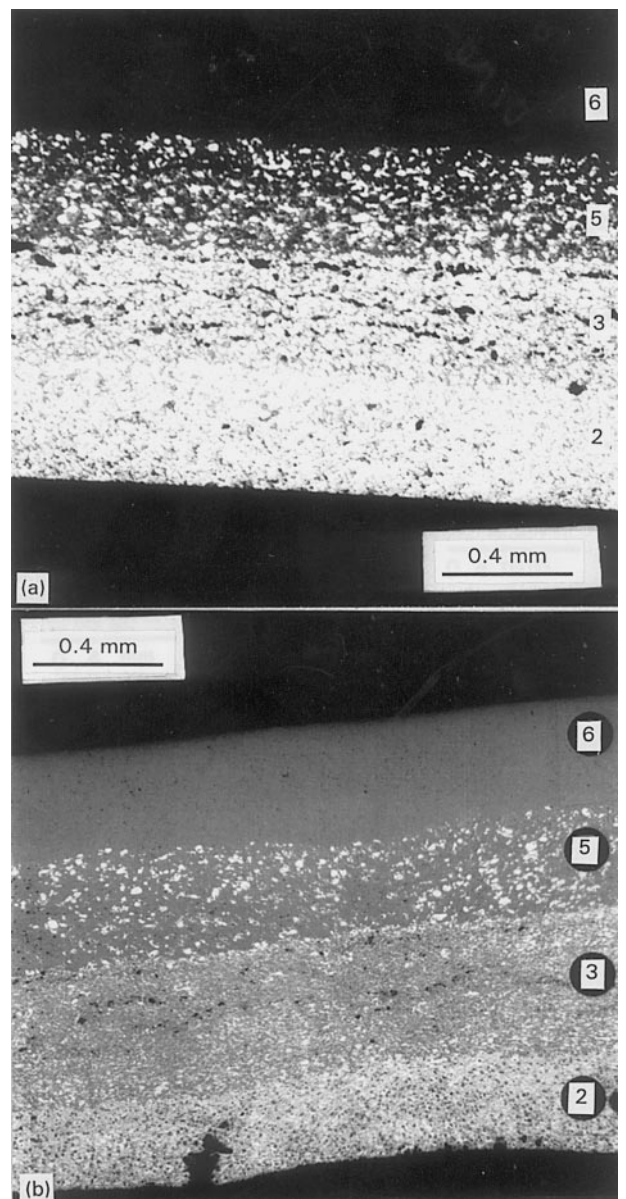


Figure 8 Optical micrograph of a cross-sectional area of a Al/SiC FGM; a) pyrolyzed at 550 °C and b) 1000 °C. Mix numbers correspond to Table VIII.

1000 °C. The composite appears to be strong, well-bonded between layers, and nearly fully dense at the SiC side. Several different Al/SiC symmetrical FGM composite configurations were also explored. Two sandwich geometries were made, one having pure Al on both outer faces and gradually changing in composition to SiC rich in the middle of the composite after its pyrolysis at 250 °C for 1 h and 550 °C for 5 h (Fig. 9a). The other sandwich was made with the SiC faces on the outside and a gradual change to Al rich

TABLE VII Cu/PCS/SiC powder mixes for the solid substrate

| Mix No | PCS ^a /SiC/Cu molar ratio | Nicalon [®] PCS wt% | SiC (- 600 mesh) wt % | Cu (- 325 mesh) powder wt % |
|--------|--------------------------------------|------------------------------|---------------------------|-----------------------------|
| 1 | 10:0:90 | 9.2 | 0 | 90.8 |
| 2 | 10:90:0 | 12.5 | 85.8% SiC; 1.7% B [32] | 0 |

^a Based on Si

TABLE VIII Al/PMS/SiC powder mixes

| Mix | PMS ^a /SiC/Al molar ratio | PMS [34] wt % | SiC (< 1 μm) wt % | Al (– 325 mesh powder wt % |
|-----|--------------------------------------|----------------|-------------------|----------------------------|
| 1 | 0:0:100 | pure Al powder | | |
| 2 | 10:0:90 | 15.3 | 0 | 84.7 |
| 3 | 10:10:80 | 14.6 | 13.4 | 72.0 |
| 4 | 10:20:70 | 14.0 | 25.7 | 60.3 |
| 5 | 10:50:40 | 12.5 | 56.8 | 30.7 |
| 6 | 10:90:0 | 12.7 (PCS) | 87.3 | 0 |

^a Based on Si

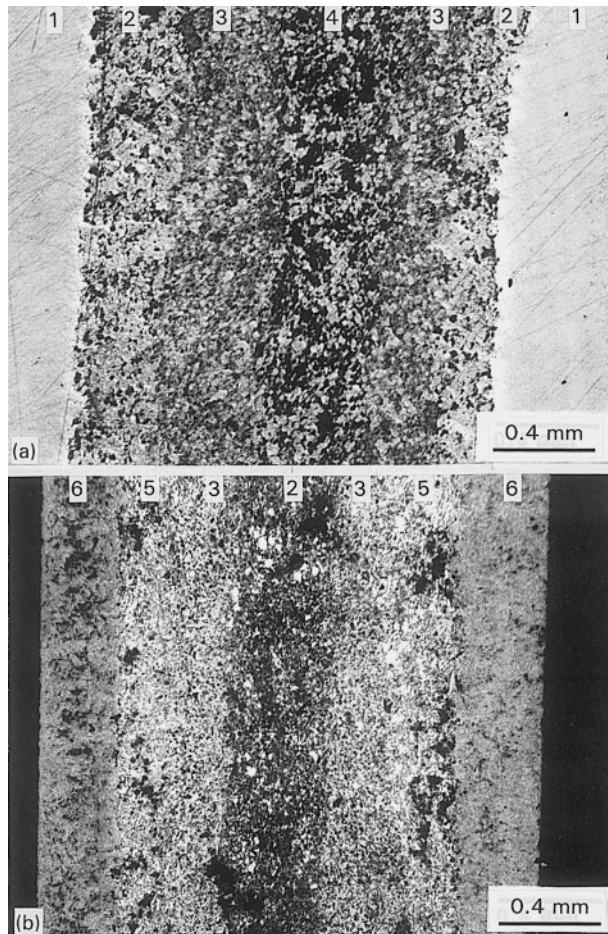


Figure 9 Optical micrograph of a cross-sectional area of a sandwich A/SiC FGM: a) pyrolyzed at 550 °C with Al outer skins and b) pyrolyzed at 1000 °C with SiC outer skins. The mix numbers correspond to Table VIII.

domains towards the middle after its pyrolysis at 1000 °C for 3 h (Fig. 9b). Some of the new crystalline phases obtained in the Al-FGM from the reaction between the polymer and Al metal were Si and Al₄C₃ as recognized by X-ray powder diffraction [29].

It was observed that the per cent shrinkage of ceramic/preceramic polymer parts is nearly linearly related to the weight per cent of preceramic polymer (Fig. 10). The density, on the other hand, is about constant. This relationship was demonstrated by employing submicron SiC powder and Co₂(CO)₈-cross-linked [35] polycarbosilane (Nicalon® precursor) in various amounts (Fig. 10). An average density of 2.58 g cm⁻³ was obtained.

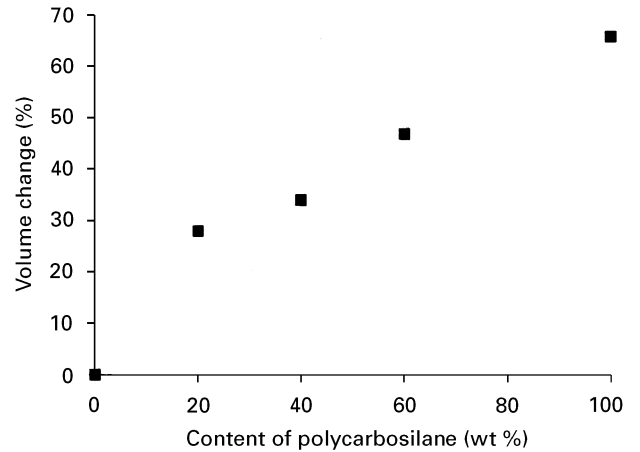


Figure 10 Shrinkage control by ceramic precursors; percentage volume shrinkage versus PCS content.

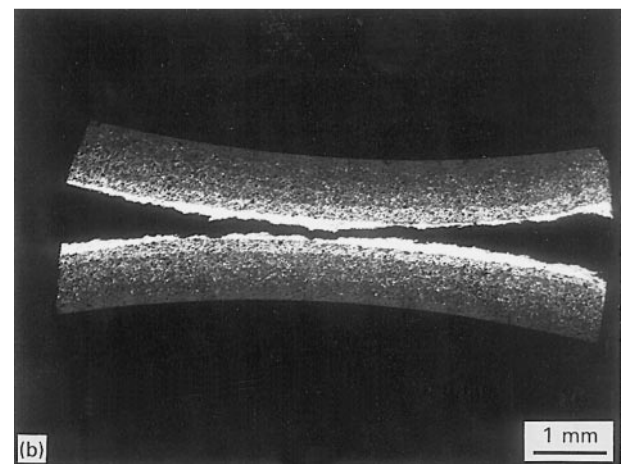
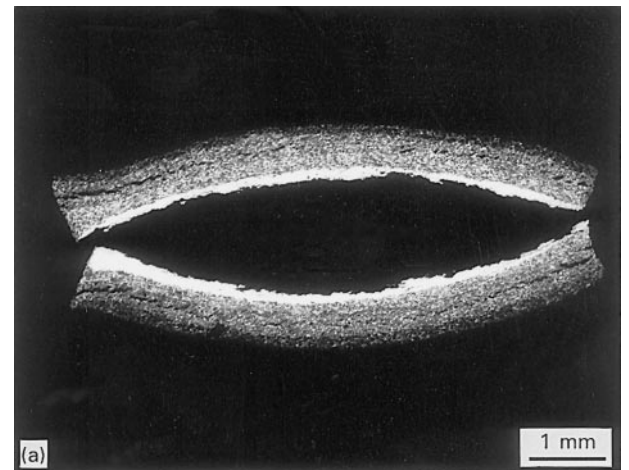


Figure 11 Optical micrographs of cross-sectional area of Cu/SiC sandwich FGM composites. The following layers (mix numbers) were overlaid: a) 7, 6, 5, 4, 3, 1, 3, 4, 5, 6, 7 (Table VI); b) 6, 5, 4, 3, 2, 1, 2, 3, 4, 5, 6 (Table IX).

TABLE IX Cu/PCS/SiC powder mixes with varying PCS content

| Mix No. | PCS ^a /SiC (1 μm)/Cu molar ratio | Nicalon [®] PCS ^b wt % | SiC (< 1 $\mu\text{m}</math>) wt %$ | Cu (– 325 mesh) powder wt % |
|---------|---|--|-------------------------------------|-----------------------------|
| 1 | 0:0:100 | pure Cu powder | | |
| 2 | 8:20:72 | 7.8 | 13.7 | 78.5 |
| 3 | 14:36:50 | 15.4 | 26.9 | 57.7 |
| 4 | 19:52:29 | 22.7 | 39.6 | 37.7 |
| 5 | 24:62:14 | 29.6 | 51.9 | 18.5 |
| 6 | 31:69:0 | 40.0 | 60.0 | 0 |

^a Based on Si

^b Crosslinked with $\text{CO}_2(\text{CO})_2^{\frac{2}{3}}$ [35]

Shrinkage control in FGM composites is an essential feature in their preparation process, especially when powders of different particle size are joined by a gradient as in the case of Cu ($\sim 10 \mu\text{m}$) and SiC (< 1 μm). It has been observed that with a constant amount of binder the highest shrinkage takes place on the Cu side and lowest on the SiC side. This shrinkage is well visible on a cross-sectional view of a sandwich composite (Fig. 11a). It appears that if the amount of polymeric ceramic precursor is continuously increasing from the higher shrinkage domain (Cu) to the lower shrinkage domain (SiC), the deformation due to shrinkage would be reversed. An example of such shrinkage control is portrayed by a symmetrical sandwich composite of SiC and Cu, a cross-sectional view of which is depicted in Fig. 11b. The current shrinkage control mechanism does not require incorporating various sizes of ceramic particles as is conventionally practiced [5, 6].

4. Conclusion

Polymeric ceramic precursors prove to be very effective substitutes for organic binders in the preparation of FGMs. This novel process of FGM preparation avoids the debinding step (removal of organic binder) used in conventional wet P/M. It also introduces a means for shrinkage control by blending various amounts of a polymeric ceramic precursor into individual FGM layers. Shrinkage may also be controlled through the incorporation of precursors which give various ceramic residue yields on pyrolysis (i.e., shrinkage is inversely proportional to ceramic residue yield), or gradually changing the nature of the polymeric binder used (i.e., a liquid binder results in less shrinkage than a solid binder). The current FGM process may further be extended to rapid prototyping applications such as 3-d printing [36–38].

References

1. K. SUGANUMA, T. OKAMOTO, M. SHIMADA and M. KOIZUMI, *J. Amer. Ceram. Soc.* **66** (1983) C-117.
2. M. KOIZUMI, *Ceram. Eng. Sci. Proc.* **13** (1992) 333.
3. N. NAKAHASHI, M. SHIROKANE and H. TAKEDA, *Surface* **24** (1986) 595.
4. J. M. HOWE, *Inter. Mater. Rev.* **38** (1993) 233.
5. A. YOSHITAKE, M. TAMURA, I. SHIOTA and M. NIINO *Space Applications of Advanced Structural Materials*, Proceedings of an international symposium; European Space Agency, Noordwijk, Netherlands, (1990) p. 103.
6. M. TAKEMURA, T. HYAKUBA, A. YOSHITAKE, M. TAMURA, M. NIINO and A. KUMAKAWA, *Ceram. Trans.* **34** (1993) 271.
7. “Functionally Graded Structural Materials” MIT Workshop, Cambridge, MA, March 28-29, 1994.
8. A. BISHOP, C.-Y. LIN, M. NAVARATNAM, R. D. RAWLINGS and H. B. McSHANE, *J. Mater. Sci. Lett.* **12** (1993) 1516.
9. K. ATARASHIYA, K. KUROKAWA and N. TADAO, *Ceram. Eng. Sci. Proc.* **13** (1992) 400.
10. R. G. FORD, *Mater. Process. Rep.* **7** (1992) 1.
11. S. SAMPATH and H. HERMAN, *J. Met.* **45** (1993) 42.
12. L. M. SHEPARD, *Amer. Ceram. Soc. Bull.* **71** (1992) 617.
13. “Combustion and Plasma Synthesis of High Temperature Materials” edited by Z. A. Munir and J.B. Holt (VCH Publishers, Inc., New York, 1990).
14. S. E. NIEDZIALEK, G. C. STANGLE and Y. KAIEDA, *J. Mater. Res.* **8** (1993) 2026.
15. M. NIINO, N. YATSUYANAGI, J. IKEUCHI, N. SATA, T. HIRANO and K. SUMIYOSHI, U.S. Patent 4 778 649, (1988)
16. “The Application of Combustion Synthesis in the In-Situ Production of Functionally-Graded Materials (FGM)”, H. J. Feng, J. J. Moore. In-Situ Composites, edited by M. Singh. (TMS, 1993).
17. “Proceedings of the First International Symposium, FGM ‘90” Sendai, Japan, October 1990, edited by M. Yamanouchi, M. Koizumi, T. Hirai and I. Shiota.
18. I. KVERNES, U.S. Patent 4 752 535, (1988).
19. M. NIINO, A. SUZUKI, T. HIRAI, R. WATANABE, T. HIRANO, and N. KUROISHI, U.S. Patent 4 751099 (1988).
20. T. NAGANO, Japanese Patent 02-217246, (1990).
21. T. KATAHIRA, H. MATSUZAWA and T. TSUCHIYA, Japanese patent 05-208405, (1993).
22. M. IWATA, W.-D. YI, N. HAYASHI, S. WATANABE and N. OTA, U.S. Patent 5 167 813, (1992).
23. R. M. GERMAN, “Powder Metallurgy Science”, (Metal Powder Industries Federation, Princeton N.J., 1984), p. 113.
24. J. SEMEN and J. G. LOOP, *Ceram. Eng. Sci. Proc.* **12** (1991) 1967.
25. D. MOHR, P. DESAI and T. STARR, *Polym. Prepr.* **32** (1991) 565.
26. S. T. SCHWAB, C. R. BLANCHARD and R. C. GRAEF, *J. Mater. Sci.* **29** (1994) 6320.
27. K. J. WYNNE and R. W. RICE, *Ann. Rev. Mater. Sci.* **14** (1984) 297.
28. S. YAJIMA, T. SHISHIDO and H. KAYANO, *Nature* **264** (1976) 237.
29. D. SEYFERTH and P. CZUBAROW, *Chem. Mater.* **6** (1994) 10.
30. D. SEYFERTH and P. CZUBAROW, U.S. Patent 5 455 000 (1995).
31. W. PRECHTL, *Keram. Z.* **45** (1993) 197.

32. T. MIZRAH, M. HOFFMANN and L. GAUCKLER, *Powder Met. Int.* **16** (1984) 217.
33. R. ADAMS, W. E. RHINE and H. K. BOWEN, *J. Electrochem. Soc.* **136** (1989) 3486.
34. D. SEYFERTH, T. G. WOOD, H. J. TRACY and J. L. ROBISON, *J. Amer. Ceram. Soc.* **75** (1992) 1300.
35. D. SEYFERTH, C. A. SOBON and J. BORM, *New J. Chem.* **14** (1990) 545.
36. T. WOHLERS, "Creating Parts by the Layers," Cadence, 1989, 73.
37. E. M. SACHS, M. J. CIMA, J. BREDT and A. CURODEAU, *Manufac. Rev.* **5** (1992) 117.
38. E. M. SACHS, J. S. HAGGERTY, M. J. CIMA and P. A. WILLIAMS, U.S. Patent 5 204 055 (1993).

*Received 13 November
and accepted 21 December 1995*