RECENT DEVELOPMENTS IN EXTRUSION FREEFORM FABRICATION (EFF) UTILIZING NON-AQUEOUS GEL CASTING FORMULATIONS

Greg E. Hilmas, John L. Lombardi, Robert A. Hoffman, and Kevin Stuffle
Advanced Ceramics Research, Inc.
Tucson, Arizona

ABSTRACT

Extrusion Freeform Fabrication (EFF) was shown to be an extremely versatile method for fabricating Functionally Graded Materials (FGMs) The approach is inexpensive and potentially feasible for grading between any thermodynamically compatible ceramic-metal, ceramic-ceramic, or metal-metal material combination. Several material systems were investigated in this study including alumina-304 stainless steel, zirconia-304 stainless steel, alumina-Inconel 625, zirconia-Inconel 625, alumina-nickel aluminide, zirconia-nickel aluminide, titanium carbide-Inconel 625, titanium diboride-nickel aluminide, and tungsten carbide-nickel aluminide. A controlled gradient was demonstrated between the end members for all of the above compositions. The FGMs were hot pressed to achieve near theoretical densities, providing flexural strengths as high as 1000 MPa for the zirconia-304 stainless steel FGM.

The FGM systems developed in this program have a wide variety of potential commercial and government applications including cutting tools and other components requiring wear resistant surfaces, aircraft engine and automotive engine components, light and heavy armor systems, and electrical insulators and heat-sinks for the electronics industry, to name a few.

INTRODUCTION

The main objective of this study was to utilize current novel manufacturing techniques for the fabrication of functionally graded materials (FGMs). FGMs have a graded transition in composition and are attractive as a method for taking advantage of the properties of two vastly different materials within the same body. FGMs differ from coated materials or conventional composites in that they are microstructurally inhomogeneous. The graded composition eliminates many of the problems associated with the presence of discrete interfaces in conventional composites such as poor mechanical integrity and transport losses due to low interfacial adhesion. It also can eliminate problems associated with thermal expansion mismatch which is not trivial for most high temperature applications. The use of slurry formulations combined with state-of-the-art freeform fabrication technologies would allow potential FGM compositions to be rapidly prototyped.

Solid freeform fabrication (SFF - also known as 'Rapid Prototyping') is a rapidly developing technology that has significant commercial potential [1-4]. It is a computer controlled, layer by layer, additive process where the desired part is first reduced to geometric sections through the use of Computer Aided Design (CAD) software. The method for transferring the CAD design to the fabrication of an actual component is quite complex and dependent on the SFF technology being utilized. However, the fabrication of solid, three-dimensional objects without tooling has rapidly progressed from producing simple models to producing complex functional prototypes. Parts can now be produced in a number of materials including wax, thermoplastics, thermosets, photopolymers, paper, metals, ceramics and glass fiber reinforced composites.

ACR is actively involved in developing its own Extrusion Freeform Fabrication (EFF) technology as a rapid and flexible prototyping and manufacturing process [5,6]. Two in-house systems have been developed which successfully freeform CAD designed complex parts using

polymer and ceramic engineering materials including Al_2O_3, ZrO_2, Si_3N_4 and SiC, as well as PEEK and polycarbonate thermoplastics. The technologies are also amenable to processing composite materials, e.g., short C fiber filled PEEK. The next technological breakthrough lies in gaining the ability to rapidly fabricate FGMs to be used as a screening process for evaluating potential FGM components. When a successful FGM composition is found, direct application of the technologies can be utilized to prototype functional three-dimensional parts. The goal of this study was to develop a rapid, flexible, and precise fabrication method for producing and evaluating potential FGMs. Nine different ceramic-to-metal graded compositions were successfully prepared during this study, resulting in a method which appears promising as a low-cost high pay-off approach for fabricating and screening potential FGMs.

EXPERIMENTAL

Development of Polymerizable Slurries

The following eight ceramic- or metal-based polymerizable slurries were produced during this study: Al_2O_3, ZrO_2, 304 S.S., NiAl, Inconel 625, TiB_2, TiC and WC. The slurries were prepared by ball milling the respective raw powder(s) into two different acrylate monomer vehicles. The compositions of the two liquid vehicles utilized in the study are outlined in Table 1. Liquid vehicle #1 is based upon 'gel casting' formulations similar to those developed by Oak Ridge National Laboratory for injection molding [7,8]. Liquid vehicle #2, developed at ACR, was found to be the preferred vehicle for all of the starting powders, achieving the highest solids loadings with the shortest milling time. Typical solids loadings achieved for the metal and ceramic slurries were in the range of 44 to 58 vol.%. The rheological properties of the slurries were also characterized using a Brookfield Model VIII viscometer.

TABLE 1. Polymerizable Liquid Vehicles

Liquid Vehicle No.	Additive	Liquid Volume %
1	DBE (Dibasic Esters)	18.5
	Triton X-100	20.5
	HDODA	55
	TMPTA	6
2†	Propylene Carbonate	61 - 63
	N,N' - dimethylacrylamide	32.5
	Dispersant	4.5 - 6.5
	(various - see Table 2)	

† All slurries formulated with liquid vehicle #2 also contained 3 wt.% N,N'-methylenebisacrylamide with respect to N,N'-dimethylacrylamide weight. This is added as a cross-linking agent.

The curing or gelation process required to solidify the liquid slurries utilized initiators to start the free radical polymerization of the monomers contained in the slurries. Most of our work in the past has relied on peroxide-based initiators such as benzoyl peroxide (BPO) which is a common free radical initiator. BPO proved to be unstable in the presence of the transition metal powders used in this study and was believed to catalytically decompose and prematurely gel the metal filled slurries [9]. This precluded the use of BPO in any of the slurries since the ceramic slurries would come in contact with the metal slurries during extrusion. Consequently, other more chemically stable initiators had to be used. It was found through extensive testing that peroxyketal and peroxycarbonates had greater stability than BPO in the presence of the metal powders. In particular, Lupersol TBEC (Elf Atochem, Philadelphia, PA) was found to be the best in all cases and was almost completely miscible in the liquid vehicle. The initiator was added to the slurries (1.5 grams per 100 ml of slurry) just prior to extrusion.

Fabrication of FGM Billets

The next step involved the formation of 'green' billets having a graded composition between various ceramics and metals. Nine functionally graded billets were prepared including: Al_2O_3 to NiAl, ZrO_2 to NiAl, Al_2O_3 to 304 S.S., ZrO_2 to 304 S.S. FGM's, Al_2O_3 to Inconel 625, ZrO_2 to Inconel 625, WC to NiAl, TiB_2 to NiAl, and TiC to Inconel 625. In order to produce FGMs, the EFF machine was configured with dual extrusion cylinders having separate slurry reservoirs for the individual ceramic and metal slurries. The flow of the individual slurries was passed through a Y-block, into a small mixing head containing an in-line static mixer, and out through a deposition needle. The extrusion head then swept out the designed path while depositing the liquid slurries to build up the 3-dimensional FGM body. The desired composition at each point was controlled in the CAD package by proportioning the rate of flow from the two extruders utilizing computer control. All of the FGM billets were ~1 cm thick in the green state and contained 4 - 6 graded layers plus two layers of each end member.

The 'green' FGM billets were subsequently thermally gelled and loaded into a graphite die lined with boron nitride. The graphite die was then placed into a binder burn-out furnace and heated at ~1°C/min. to 500°C and held for 2 hours in a flowing nitrogen atmosphere in order to pyrolyze the organic binder in the billets. The billets were subsequently induction hot pressed according to the following heating schedule and the hot pressing conditions outlined in Table 2:

1.) Heat at 20°C/min. from room temperature to 1100°C
2.) Heat at 10°C/min. to the final hot pressing temperature
3.) Apply load (25 MPa) at 1000°C
4.) Remove load after 60 min. at final hot pressing temperature
5.) Cut furnace power for cool down (~15°C/min.).

Table 2. Hot Pressing Condition for the FGM Billets

FGM Billet	Hot Pressing Temperature (°C)	Hold Time at Temp. (min.)	Atmosphere
Al_2O_3-304 S.S.	1250	60	800 torr Ar
ZrO_2-304 S.S.	1250	60	800 torr Ar
Al_2O_3-NiAl	1350	60	800 torr Ar
ZrO_2-NiAl	1350	60	800 torr Ar
Al_2O_3-Inconel 625	1175	60	800 torr Ar
ZrO_2-Inconel 625	1175	60	800 torr Ar
TiC (Ni,Mo)-Inconel 625	1175	60	800 torr Ar
TiB_2 (Ni)-NiAl	1350	60	800 torr Ar
WC (Co)-NiAl	1350	60	800 torr Ar

The final hot pressing temperatures were restricted by the melting points of the individual metals in order to avoid flow of the metals out of the graphite die as well as to prevent reactions with the graphite. In general , hot pressing was accomplished at temperatures 200 degrees below the melting temperature of the metals. Unfortunately, this had the potential to limit the densification of the ceramic phases. ZrO_2 is known to hot press to near theoretical density at low temperatures (e.g., 1250°C) making it an attractive ceramic constituent for these particular FGM compositions.. However, Al_2O_3 does not densify as readily at these low temperatures (typically requiring >1450°C hot pressing temperatures) and was therefore a less attractive ceramic constituent for the FGM compositions being studied. The TiC, TiB_2, and WC ceramics required some liquid phase sintering aids in order to achieve near theoretical densities at these low hot pressing temperatures. Since these ceramic materials have been extensively studied as potential and even current production cutting tool materials, a survey of the literature revealed a variety of metallic additions which would act as suitable liquid phase sintering additives allowing these ceramics to be densified in the range of 1200 to 1400°C [10-16]. It was decided to utilize 8 wt.%

Ni + 2 wt.% Mo additions for the TiC, a 10 wt.% Ni addition for the TiB_2, and a 6 wt.% Co addition for the WC.

Materials Evaluation

The experimental densities for the FGM billets were determined utilizing the Archimedes' density method, taking the average of three samples. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed at the University of Arizona using a Hitachi 2460N electron microscope equipped with a Noran EDS system equipped with a light element window and a silicon/lithium detector. Cross-sections of the billets were cut into ~5 mm x 5 mm squares, mounted in epoxy, and polished to a 1 μm diamond finish followed by a brief polish with a 0.05 μm SiO_2 slurry. The samples were then coated with a conductive gold-palladium coating and observed in the SEM at 25 kV. Preliminary mechanical property evaluations were performed in the form of four-point flexural strength measurements. Flexure bars (~4 mm wide x 4 - 5 mm long x 45 mm long) were cut and ground from each of the FGM billets.

RESULTS

Development of Polymerizable Slurries

The only powder which presented some difficulties in working with and producing a workable slurry was the Inconel 625. Using liquid vehicles #1 and #2, slurry formulations were attempted with the Inconel powder but were not successful in the first several trials. The Inconel had a tendency to settle rapidly and not remain well dispersed. It also exhibited a strong shear thinning behavior which led us to believe that the surface chemistry of this particular powder was quite complex compared to the other powders. We eventually solved both the surface chemistry and settling problems by utilizing two dispersants simultaneously and a 360,000 molecular weight polyvinylpyrrolidone additive as a thickening agent, respectively.

All of the ceramic and metal slurries were found to exhibit a thixotropic rheology whereby the apparent slurry viscosity rapidly decreased with increasing shear rate. Thixotropic rheology is a beneficial characteristic of the EFF slurries since it enables low pressure extrusion and accurate deposition of the freeformed material with minimal layer spreading once the slurry is deposited.

As an example, figure 1 below depicts the typical rheological behavior for the Al_2O_3 EFF slurry developed in this study. From the plot it can be seen that the slurry is highly thixotropic such that a fourfold difference in apparent slurry viscosity is observed at high versus low shear rates. The viscosity plot was fit to the Cross rheological model [17] and an expression relating this curve fit is given below:

$$\eta = 7750 \dot{\gamma}^{-0.715}$$

where η is the apparent viscosity and $\dot{\gamma}$ is the shear rate. The -0.715 exponent in the expression signifies that the fluid is strongly shear thinning and is similar to values observed for other highly thixotropic fluids (i.e. gel toothpaste)[18]. This suggests that EFF compatible slurries should typically have Cross rheological model exponents of similar value.

Fabrication of FGM Billets

The FGM billets typically came out of the hot press with a slight bow to them, concave on the metal side and convex on the ceramic side. Despite the gradient from ceramic-to-metal through the thickness of the billet, the pure metal side of the billets had a thermal expansion coefficient 2 to 3 times that of the pure ceramic side. In effect, the metal side contracted more than the ceramic side upon cooling instead of remaining flat and placing the ceramic into compression, therefore the billets would warp slightly. This placed the ceramic side of the billets in tension. For the NiAl
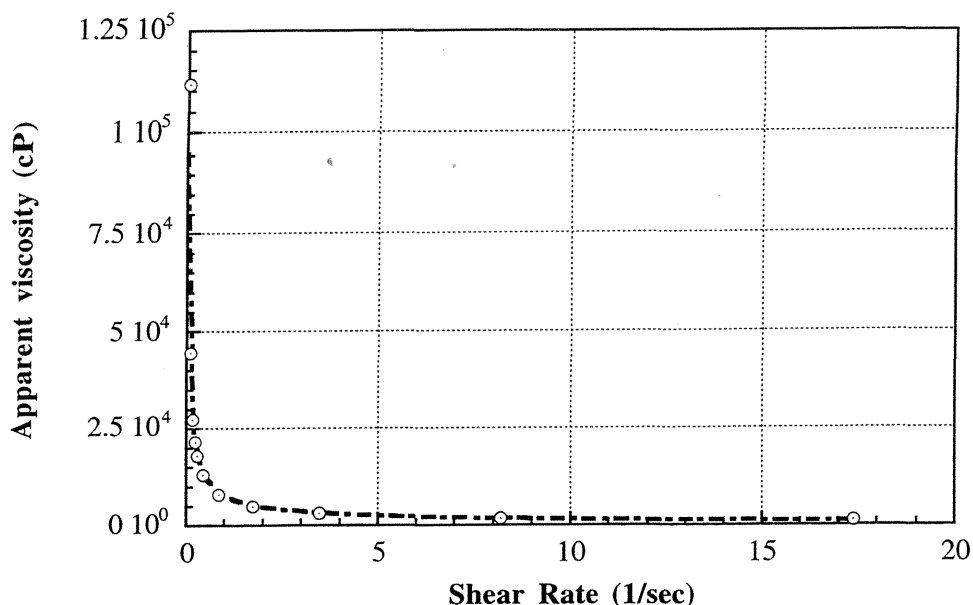
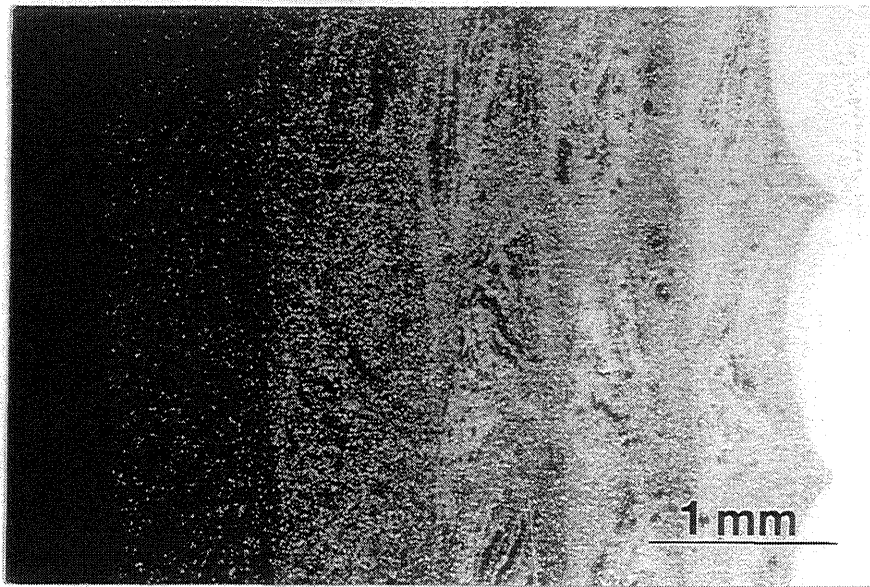**Figure 1.** Apparent viscosity vs. shear stress for the Al_2O_3 slurry.

containing FGM billets, the cooling stresses led to cracks on the ceramic side of the billets. However, these were through-thickness cracks and not delamination cracks. For the ZrO_2-NiAl and Al_2O_3-NiAl billets the pure ceramic side was able to be ground away without propagating the surface cracks and flexural bars could be produced for mechanical testing. For the WC(Co)-NiAl and the TiB_2(Ni)-NiAl billets the cracks had already propagated through the billets after hot pressing, leaving pieces too small for the fabrication flexure bars but large enough for SEM analysis.

Materials Evaluation

The SEM results for two representative FGM billets are shown in Figures 2 and 3. The majority of the FGM billets did not show any intermixing between the graded layers during hot pressing. The only exception was the TiC(Ni, Mo)-Inconel 625 billet which was completely intermixed after hot pressing to the point where individual graded layers were impossible to determine. The result still demonstrated a uniform transition between ceramic and metal, but there remained a definite segregation of the end members. The ZrO_2-304 S.S., Al_2O_3-NiAl, and ZrO_2-Inconel 625 FGM billets contained cracks running perpendicular to the graded layers in their ceramic end member. We believe these cracks to be the result of tensile residual stresses generated during the cooling cycle after hot pressing.
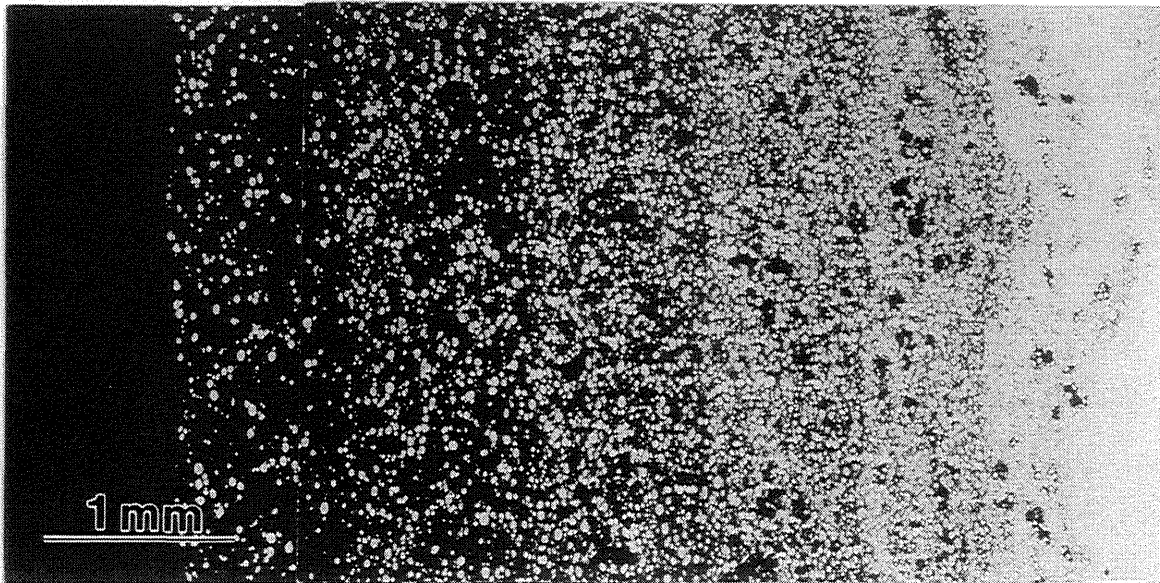
The majority of the FGM billets achieved in the range of 94-97% of their theoretical density with the Al_2O_3-304 S.S. billet being the lowest at 87% of theoretical. The theoretical densities were based on 50 vol.% each of the two end members which is what the EFF software program was designed to produce during extrusion. The experimental density data for the FGM's fits well with what was observed in the SEM and the hot pressing temperature limits imposed on the ceramic phases. For the most part, the pure metal end members are near 100% of their theoretical density, while the pure ceramic end members were still reasonably dense (84-94%) despite the low hot pressing temperatures.

For most of the FGMs, the low ceramic densities coupled with a tensile residual stress state on the ceramic side, developed during cooling from the hot pressing temperature, led to low strengths (typically 100-160 MPa) when the four-point bend tests were performed with the ceramic side as the tensile surface. However, when the metal side was tested as the tensile surface, the strength values always increased. In fact, for the ZrO_2-304 S.S. and Al_2O_3-304 S.S. FGM billets the strengths, ~1000 and 780 MPa, respectively, were higher than the theoretical strengths of most of

Al$_2$O$_3$ ———————————————————→ **304 SS**

Figure 2. SEM micrograph of a cross-section of the Al$_2$O$_3$-304 Stainless Steel FGM billet, a plot demonstrating its composition profile (experimentally vs. theoretically determined), and EDS spectra from the end members of the FGM.

Al$_2$O$_3$ ———————————————————→ **Inconel 625**

Figure 3. SEM micrograph of a cross-section of the Al$_2$O$_3$-Inconel 625 FGM billet, a plot demonstrating its composition profile (experimentally vs. theoretically determined), and EDS spectra from the end members of the FGM.

the end members. Figures 4 shows a load-deflection curve for the ZrO$_2$-304 S.S. FGM system with the 304 S.S. in tension. The ceramic actually spalled off the compressive side of the bars prior to failure during many of the flexure tests. When the flexure bars were tested with the

ceramic side in tension, the crack would pop in on the tensile side of the bar at a low load but would then be deflected several times by the ceramic-metal graded layers. This resulted in tests that showed materials with low strengths but having an extremely high work-of-fracture. In the end, the bars were visibly bent and cracked but remained intact.

The remaining FGM compositions were linearly elastic to failure, although the ZrO_2-Inconel 625 FGM flexure bars showed similar behavior to the ZrO_2-304 S.S. bars with strengths approaching 400 MPa for the metal side. The FGM billets containing NiAl as the metal side all exhibited low strengths. Polycrystalline NiAl is known to be a brittle metal with typical tensile strengths of only 250 MPa for this stoichiometric composition.
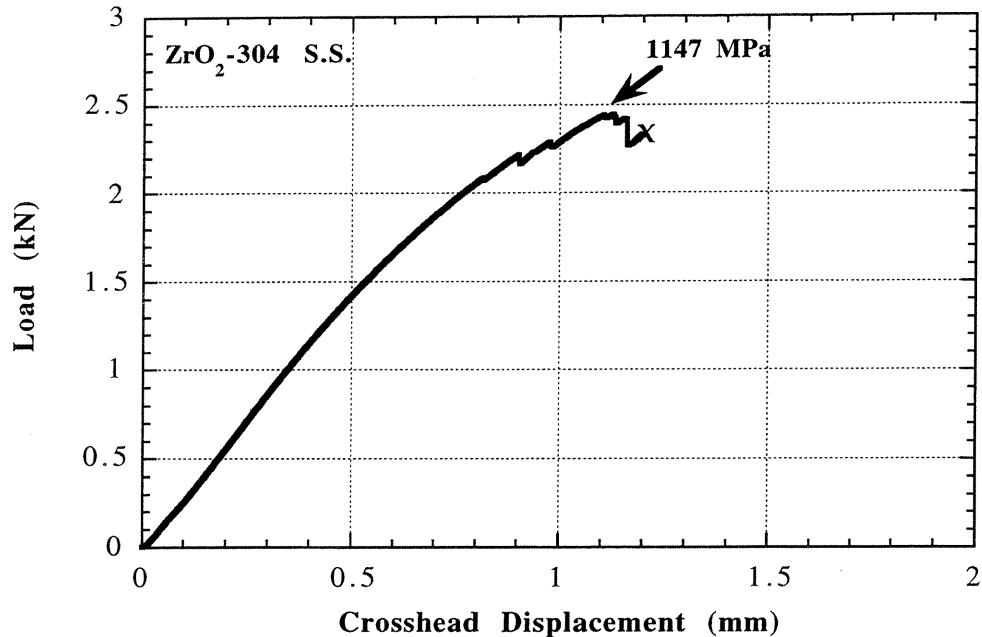

Figure 4. Load-deflection curve for a ZrO_2-304 S.S. four-point bend test bar The bar was tested with the 304 S.S. side of the bar in tension and the ZrO_2 side in compression.

CONCLUSIONS

This study demonstrated that extrusion freeform fabrication (EFF) is a versatile method for the fabrication of functionally graded materials (FGMs). While not all of the FGM billets turned out to be crack-free and 100% dense, there were some very promising FGM systems with intriguing mechanical properties. As an example, the ZrO_2-304 S.S. system achieved ~95% of its theoretical density and yielded strengths greater than 1000 MPa. We firmly believe that careful control of the hot-pressing conditions (slower cooling from the sintering temperature) and some lower temperature sintering aids for the ceramic phases would ultimately result in crack-free and dense FGM structures for most of the rest of the systems. The nine different ceramic-metal FGMs produced in the program clearly shows the technology as a viable method for both screening and producing potential FGM systems and components.

ACKNOWLEDGMENTS

REFERENCES

1. P. Jacobs, "Fundamentals of Stereolithography," Society of Manufacturing Engineers, Dearborn, MI. 1992.
2. Proceedings of the Third European Conference on Rapid Prototyping and Manufacturing, P.M. Dickens, Ed., University of Nottingham, England. 1994.
3. Solid Freeform Fabrication Symposium, H.L. Marcus, J.L. Beaman, J.W. Barlow, D.L. Bourell, and R.H. Crawford, Eds., University of Texas, Austin, TX. 1994.
4. Solid Freeform Fabrication Symposium, H.L. Marcus, J.L. Beaman, J.W. Barlow, D.L. Bourell, and R.H. Crawford, Eds., University of Texas, Austin, TX. 1993.
5. P. Calvert, R. Crockett, J. Lombardi, J. O'Kelley, and K. Stuffle, "Extrusion Methods for Solid Freeform Fabrication," pp. 50-55, in Solid Freeform Fabrication Symposium, H.L. Marcus, J.L. Beaman, J.W. Barlow, D.L. Bourell ,and R.H. Crawford, Eds., University of Texas, Austin, TX. 1993.
6. K. Stuffle, A. Mulligan, P. Calvert, and J. Lombardi, "Solid Freebody Forming of Ceramics from Polymerizable Slurry," pp. 60-63, in Solid Freeform Fabrication Symposium, H.L. Marcus, J.L. Beaman, J.W. Barlow, D.L. Bourell, and R.H. Crawford, Eds., University of Texas, Austin, TX. 1993.
7. M. A. Janney, "Method for Molding Ceramic Powders," U.S. Patent No. 4 895 194, Jan. 16, 1990
8. A. C. Young, O. O. Omatete, M. A. Janney, and P. A. Menchofer, "Gel Casting - A New Ceramic Forming Process, *J. Am. Ceram. Soc.*, **74** [3], 612-618 (1991).
9. G. Odian, *Principles of Polymerization*, 3rd ed. - pp. 219-222, John Wiley & Sons, New York, NY, 1991.
10. A. R. Bobrowsky, "The Applicability of Ceramics and Ceramals as Turbine-Blade Materials for the Newer Aircraft Power Plants," *Trans. ASME*, **8**, 621-629, 1949.
11. N. M. Parikh and M. Humenik, Jr., "Cermets: II, Wettability and Microstructure Studies in Liquid-Phase Sintering," *J. Am. Ceram. Soc.*, **40** [9], 315-320, 1957.
12. C. F. Yen, C. S. Yust, and G. W. Clark, "Enhancement of Mechanical Strength in Hot-Pressed TiB_2 Composites by the Addition of Fe and Ni," *ORNL Technical Report*, CONF-81093-2, Oak Ridge, TN, 1979.
13. M. K. Ferber, P. J. Becher, and C. B. Finch, "Effect of Microstructure on the Properties of TiB_2 Ceramics," *J. Am. Ceram. Soc.*, **66** [1], C2-C3, 1983.
14. V. J. Tennery, C. B. Finch, C. S. Yust, and G. W. Clark, "Structure-Property Correlations for TiB_2-Based Ceramics Densified using Active Liquid Metals," pp. 891-909 in Science of Hard Materials. Edited by R. K. Viswnadham, D. J. Rowcliffe, and J. Gurland. Plenum Press, New York, NY, 1983.
15. R. F. Snowball and D. R. Milner, "Densification Processes in the Tungsten Carbide-Cobalt System," *Powder Metal.*, **11** [21], 23-40, 1968.
16. D.-Y. Kim and A. Accary, "Mechanisms of Grain Growth Inhibition During Sintering of WC-Co Based Hard Metals," pp. 235-244 in Materials Science Research, Vol. 13, Sintering Processes. Edited by G. C. Kuczynski. Plenum Press, New York, NY, 1980.
17. H. A. Barnes, pp. 116-119 in An Introduction to Rheology, Elsevier, Amsterdam, 1989.
18. P. J. Whitcomb and C. W. Macosko, *J. Rheology*, **22**, 493-505, (1978).