Fused Deposition of Ceramics and Metals : An Overview

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Fused Deposition of Ceramics (FDC) and Metals (FDMet) are SFF techniques, based on commercial FDM™ technology, for rapid fabrication of functional ceramic and metal parts from powder/binder materials. This work demonstrates the possibility of applying FDC and FDMet to a variety of ceramic and metal particulate systems for fabrication of components/parts/devices for wide ranging applications such as tooling, investment casting cores and shells, structural and functional components, etc. Several particulate ceramic and metal systems have been explored for FDC and FDMet. The particulate systems explored vary in particle size from nano-crystalline (WC-Co) to coarse (>100 μm SiO_2) particles. The material systems explored for FDC and FDMet vary from conventional ceramic and metal systems such as SiO_2 and stainless steel to advanced materials such as Si_3N_4 and PZT. FDC and FDMet of such a variety of material systems using a commercial FDM™ system has been made feasible by development of a unique series of binders, as well as optimized FD processing, binder removal techniques and sintering conditions.

I. Introduction

SFF techniques have been commercialized for fabrication of polymer and wax parts for design verification and form and fit [1]. Wax and polymer parts made by SFF have also been used to produce metal and ceramic parts using a two-step process. Once a wax or polymer part is built by SFF, it serves as the positive for investment casting of metallic alloys [1]. Also the wax and polymer materials are being used to make molds for ceramic slurry and gel casting [2,3]. The direct production of metallic or ceramic prototypes for functional applications and testing is currently a major focus in the field of SFF [1, 4-7].

Most of the SFF techniques used for fabrication of metal and ceramic parts employ polymeric binder systems to bond the ceramic or metal particles together to form a green part [1,3-7]. Once a green part is formed by the SFF technique, further processing follows the approach of conventional green forming techniques, such as powder injection molding. The fabricated green part is processed to remove the binder from the part and then sintered or infiltrated with a lower melting second phase. However, fabrication of green metal or ceramic parts by various SFF techniques have been far from trivial. In the SFF techniques, effort is required in developing the proper binder chemistry and often tailoring the *as-received* commercial ceramic or metal powders to allow SFF processing. Once the binder and particulate systems have been developed, the SFF processing conditions are optimized to fabricate high quality green bodies.

This article discusses the results of a new SFF technique, called Fused Deposition of Ceramics (FDC) and Metals (FDMet), which has been applied to a wide range of ceramic and metal systems [3,6,7]. FDC and FDMet are based on an existing Fused Deposition Modeling (FDM™) technology, commercialized by Stratasys Inc. for polymers and waxes [8,9].

II. Fused Deposition of Ceramics (FDC) and Metals (FDMet)

Fused Deposition of Ceramics (FDC) and Metals (FDMet) is being developed to create functional ceramic and metal components using ceramic or metal powders mixed with organic binder systems. The mixed powder-binder feedstock is extruded into filaments of 0.070" nominal diameter, which are then used as the feed material for fabrication of green ceramic or metal parts using a commercial FDM™ system. The FDC/FDMet green part is then subjected to conventional binder removal and sintering processes to produce fully dense structural ceramic/metal components. As in the case of any manufacturing process, there are several inter-related process variables which determine the success and quality of parts fabricated by FDC or FDMet.

Successful FDC/FDMet processing starts with fabrication of filaments of uniform diameter (0.070" ± 0.001") to be used as feed material in the FD hardware. However, for a filament material to be suitable for FD processing, it must possess certain thermal and mechanical properties [9,10]. The key variables that require careful attention and simultaneous optimization in developing the filaments for FDC/FDMet processing are: viscosity and adhesion behavior of the material, and the flexural modulus and strength of the filaments. Based on the constraints imposed by these variables, a series of thermoplastic binders have been developed to enable FDC/FDMet processing. These binders, called the RU binder series, are four component systems - an elastomer, tackifier, wax, and a polymer. The amount of each component was tailored to achieve appropriate viscosity, adhesion behavior, flexibility and stiffness in the green filaments [10]. Appropriate tailoring of these components and selection of a suitable surfactant for a specific particle system have enabled FDC/FDMet processing of several ceramic and metal systems.

FDC/FDMet using the RU series of binder has been demonstrated for Si_3N_4, fused SiO_2, Al_2O_3, lead zirconium titanate (PZT), stainless steel and WC-Co. In each of these particle systems, initial trials for FD were done using a basic composition of the RU binder series, called RU1, which has 30% wax, 35% polymer, 20% elastomer, and 15% tackifier by weight. Further optimization of the binder from the RU1 composition was done, if needed, to achieve the needed flexibility in the filaments to allow automated FD processing or to lower the viscosity to enable FDC/FDMet processing. As reported elsewhere [10], the binder chemistry has been nearly optimized for Si_3N_4 to yield flexible and continuous filaments. FDC/FDMet of other materials has been demonstrated without much variation in the binder composition from the RU1 chemistry. Mixing of the ceramic or metal powder with the binders was done in a torque rheometer mixer to achieve 50 to 65 volume % particle loading. The particle loading achieved in a specific particulate system depends on the particle size and particle size distribution and whether or not a suitable surfactant is used. These factors determine the viscosity of the mixed feedstock which should not exceed a certain limit which will prevent FD processing. Filaments were fabricated from the mixed feedstock using a capillary rheometer or a single screw extruder [10].

Once suitable filaments were fabricated, FDC/FDMet processing was done using a commercial FDM™ system, 3D Modeler™, hardware and software. Build strategies used in the FDC/FDMet were largely the same as those for FDM™ processing of wax and polymers. However, some novel build strategies were developed and implemented to prevent and eliminate property limiting internal defects which arise in conventionally processed FD parts [11]. The choice of slice thickness and road widths for FDC/FDMet were determined by the nozzle diameter, which in turn is determined by the maximum particle size in the specific ceramic or metal system. The FDC/FDMet green parts were further processed to remove the RU binder completely. The binder removal process is done in two stages such that the RU binder is completely removed without any cracking or damage to the part [6,7]. The sintering of the FDC/FDMet part is done by conventional sintering operations for the specific particle system used under consideration.

FDC of Silicon Nitride

Although several ceramic and metal systems have been investigated for the FDC/FDMet processes, the most extensive work to date has been done using an *in-situ* reinforced Si_3N_4 from AlliedSignal Ceramic Components of Torrance, California. *As-received* Si_3N_4 powder coated with appropriate surfactant was used in this study with 55 volume % Si_3N_4 in the mixed powder/binder feedstock. The RU series of binder used for FDC of Si_3N_4 has been optimized to result in flexible and continuous 0.070" ± 0.001" diameter filaments fabricated by single screw extrusion [10]. FDC of Si_3N_4 has been done successfully using novel build strategies employed with a commercial FDM™ system to result in sintered parts with physical and mechanical properties comparable to those obtained by conventional processing of Si_3N_4 [7]. FDC of Si_3N_4 has also been demonstrated by fabrication of complex engineering components. Details of the FDC process for Si_3N_4 and their results can be found elsewhere [7].

FDC of Fused Silica

Fused silica, alumina, and zircon are commonly used for fabrication of investment casting tooling. Traditionally, investment casting ceramic shells and cores are manufactured using machined positive patterns of the parts or by injection molding of the actual cores and shells. SFF techniques have been used directly or indirectly for fabrication of investment casting cores and shells. Indirect fabrication involves SFF fabrication of the positive pattern from wax and polymers for the mold. The wax or polymer positive is then used to form a ceramic shell by sequential dipping of the pattern in a ceramic slurry [1]. The wax or polymer is then melted out of the shell followed by firing the shell. Direct fabrication of such ceramic shells and cores for investment casting has been commercialized using the 3D Printing process [5]. The study reported here demonstrates the feasibility of using the FDC process for fabrication of silica parts for investment casting with properties comparable to parts fabricated by conventional core making techniques.

A commercial grade silica powder used for injection molding of investment casting cores by Certech Inc. of Woodridge, New Jersey, was used for FDC in this study. The particle size of the *as-received* silica powder was in the range of 0.01µm - 150µm, with an average particle size of 70 µm. Conventionally, injection molding of cores done by Certech uses 68 volume % silica such that linear shrinkage during firing is limited to ~1%, with a final density of ~70% of theoretical density. In order to have comparable shrinkage and final density in the FDC parts, the RU1 binder was mixed with 65 volume % silica powder. Filaments fabricated by capillary and single screw extrusion were straight and stiff with insufficient flexibility for continuous winding onto a spool. A series of 0.25" X 0.25" X 2.5" bars for modulus of rupture (MOR) tests and simple core shape were fabricated by FDC, Figure 1 . After binder removal, the bars were fired at Certech Inc. at 1225°C for 6 hours, Figure 2 . MOR testing was done to evaluate the mechanical properties. The bars were also used for physical property evaluations, which are critical in determining whether or not the parts can be used for investment casting applications. These physical and mechanical properties were compared with those of injection molded samples of the same grade of silica.

As shown in Figures 3, the microstructure of fired FDC silica samples is comparable with that of fired injection molded samples with no evidence of delamination or inter-road debonding. Similarly, the physical and mechanical properties of the FDC processed samples compare very favorably with the reported properties of injection molded parts, Table I, and were within the commercial upper and lower acceptable limits reported by Certech's specification data sheet. For example, although the average cristobalite level in FDC samples is lower than those in injection molded samples, the levels are well within the acceptable limits of 20% and 7%, respectively. The starting volume fraction of silica in FDC samples is lower (65%) than that in injection molded parts (68%), while the final bulk density of both FDC and injection molded parts are similar. Therefore, the linear shrinkage observed in FDC samples was slightly higher. Since the number of FDC samples tested was few (10) in comparison to injection molded samples used for reporting data in product data sheet, the standard deviation for the properties in FDC samples (shown in parenthesis in Table I) indicate a wider spread in the FDC values compared to the injection molded samples. However, this study demonstrates that FDC is a viable SFF technique for direct fabrication of investment casting ceramic cores and shells using commercial grade powders with resulting properties comparable to those of conventionally processed parts.

FDC of Piezoelectric ceramics

Piezoelectric materials have the ability to convert electrical energy into mechanical energy or conversely convert mechanical energy into electrical energy. The applications for devices from these materials include transducers, microphones, phonographic pick-ups, speakers, accelerometers, strain gages, ignitors, and various medical diagnostic systems. Several ceramics exhibit piezoelectric behavior, with lead zirconium titanate (PZT) being the most extensively used. Piezoelectric ceramic/polymer composites, consisting of a piezoelectric ceramic, such as PZT, in an inactive polymer, have shown superior properties when compared to monolithic single phase materials. The piezoelectric properties have been vastly improved over the last two decades through fabrication of numerous innovative structures [12]. However, most of the processing techniques lack the flexibility of fabricating novel structures.

SFF techniques, specifically FDC in this study, provide an opportunity to control the fabrication of these complex structures as material is deposited one volume element at a time only in desired locations and is directly controlled by the computer through the component CAD file [1]. Such flexibility, of SFF in general and FDC in particular, allows deposition of material at a very fine scale only in desirable locations and leaving the other areas unfilled [3]. Once the desirable green ceramic structure of PZT is fabricated, the remaining unfilled regions are filled by the inactive polymer phase, following binder removal and sintering. Such an approach results in complex geometries of piezocomposites to be fabricated with relative ease. In this study, *as-received* spray-dried PZT powder from Morgan Matroc Inc. of Cleveland, Ohio, was used. Green PZT filaments containing 50 volume % PZT powder and 50 volume % RU1 binder with a surfactant and plasticizer was used, Figure 4. Several simple shapes with intricate internal structures, such as ladder structures, were formed using FDC, Figures 4 and 5. After binder removal and sintering of the green FDC PZT parts, the parts were infiltrated with an inactive polymer to form the final desired piezocomposites. The piezoelectric properties of the piezocomposites by FDC were measured and found to be significantly better than those reported for conventionally processed PZT composites. Further details and results on FDC of piezoceramics can be found in these proceedings [3].

FDMet of Stainless Steel

As mentioned earlier, one of the major applications of SFF technologies has been to fabricate polymer or wax positive patterns for investment casting of metallic alloys. Such an approach has been successfully adopted by automotive and aerospace industries in investment casting of critical components from metals [1]. To further maximize the benefits of SFF technologies, direct fabrication of such metal components by SFF techniques are being developed. This study demonstrates the feasibility of using FDMet for fabrication of green parts from powder stainless steel which can then be further processed by binder removal and sintering to result in a fully dense steel part.

Precipitation hardened stainless steels are commonly used in various industrial and military applications where resistance to corrosion and high mechanical performance at temperatures to 400°C are necessary. Typically these steels are available in wrought form and the parts are fabricated by conventional thermomechanical processes. The precipitation hardened steel used in this study was a 17-4PH grade (also referred as Type 630) stainless steel powder of -325 mesh particle size. Powder with 60% by volume was mixed with RU1 binder composition and extruded into stiff, straight filaments of 0.070" nominal diameter using a capillary extrusion process. Simple green stainless steel shapes were created at 110°C using the commercial FDM™ system, Figure 6. Following binder removal, the parts were sintered at 1350°C for 1 hour in a mild reducing atmosphere (H_2+N_2), Figure 7. Although sintered parts exhibit high density (92%-95% of theoretical), close examination of sintered parts reveal internal delamination and cracking in the parts. Further experiments with capillary extruded green rods (3/8" diameter) of the same composition revealed cracking and bloating occurring during the binder removal process. It is expected that once the binder removal is optimized to prevent defects, stainless steel FDMet parts with properties and microstructures comparable to that of wrought formed parts can be achieved.

FDC of WC-Co

Tungsten carbide (WC)-based composites have a good combination of properties including high hardness, toughness, and wear and abrasion resistance. These properties make them suitable for a variety of tooling applications such as metal cutting, mining, rock drilling, dies, and wear parts. The basic tungsten carbide-cobalt (WC-Co) material has been modified over the years to produce a variety of cemented carbides for these applications. Conventional powder metallurgical techniques are used for processing and fabrication for these materials. Today, new techniques are being developed to reduce costs and improve performance. One of these new technologies include synthesis and use of nanocrystalline WC-Co powders. As SFF techniques are being explored for metals and ceramics and the SFF technologies have also led to significant growth and demand in Rapid Tooling applications, it is only natural to explore SFF techniques for WC-Co.

In this study, FDC was explored as an SFF technique for fabrication of WC-Co shapes. Two different grades of commercial WC-Co powders were used in this study, nanocrystalline WC-15Co from Nanodyne, Inc. and WC-15Co from Valenite, Inc. Due to the extremely fine particle size and high density (~14 g/cm^3) of these materials, the viscosity of the RU1 binder mixed with only 50 volume% of these WC-Co was too high to allow successful FDC processing using commercial FDM™ systems. To allow successful FDC processing, the RU series binder was tailored and a suitable dispersant was developed to lower the viscosity of 50-55 volume % WC-Co loaded binder system. Initial FDC trials with the RU binder formulation and use of dispersant, indicate that it is possible to achieve high solids loading (50-55 volume%) of nanocrystalline WC-Co and attain a viscosity level low enough for FDC processing at 200°C [10]. Further development of binder and dispersant are expected to result in optimized FDC processing of WC-Co with sintered properties comparable to those of conventionally processed WC-Co.

FDC of Alumina

Alumina is a commonly used ceramic in many structural applications. FDC of alumina has been demonstrated by Lone Peak Engineering of Draper, Utah, with very much the same approach as reported here [4]. In the study by Lone Peak Engineering, FDC was done using commercial grade A-16SG alumina powders and thermoplastic binders with suitable plasticizers and dispersants. As discussed elsewhere [4], FDC processed alumina parts in the study exhibited greater than 97% theoretical density after sintering.

Conclusions

This article demonstrates that FDC and FDMet are SFF techniques which are practical for rapid fabrication of structural and functional parts/components from powder/binder mixtures. A unique series of binders developed for FDC/FDMet have been uniformly applied to a wide range of ceramic and metal systems for FD processing. The materials studied here demonstrate that *as-received* commercial powders can be readily used for FDC/FDMet with sintered parts exhibiting properties comparable to those of conventionally processed parts from the same material. By tailoring the RU series of binder and proper selection of dispersants and optimization of the FD process and binder removal procedures, different material systems can be readily developed for FDC/FDMet processing.

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Table I
Physical and Mechanical Properties of Fused Silica Processed by FDC and Injection Molding

Processing Technique	Bulk Density (g/cm^3)	Apparent Density (g/cm^3)	Porosity (%)	Absorption (%)	Modulus of Rupture (psi)	Linear Shrinkage (%)	Cristobalite Level (%)
FDC	1.58 (0.01)	2.26 (0.00)	30.0 (0.52)	19.0 (0.5)	1825 (243)	1% - 4%	11.5
Injection Molding	1.58 (0.00)	2.29 (0.01)	31.2 (0.4)	19.7 (0.3)	1788 (96)	1.53 (0.3)	16.9

Numbers in parantheses are standard deviation of the data reported.

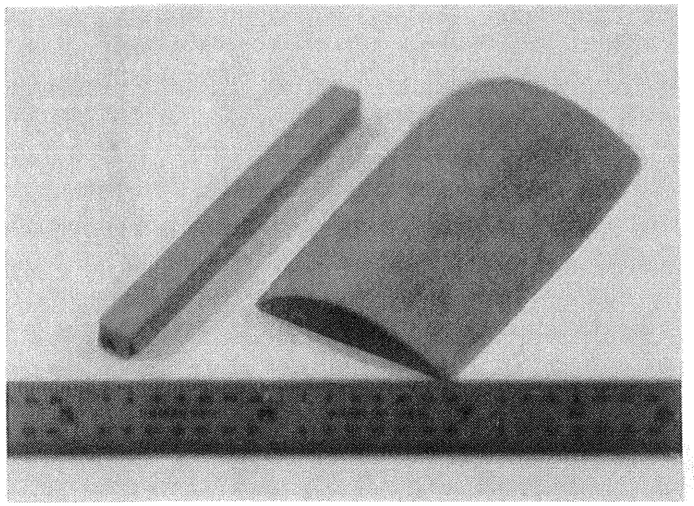

Figure 1: Green fused silica parts, a MOR bar and a section of a core for investment casting, processed by FDC.

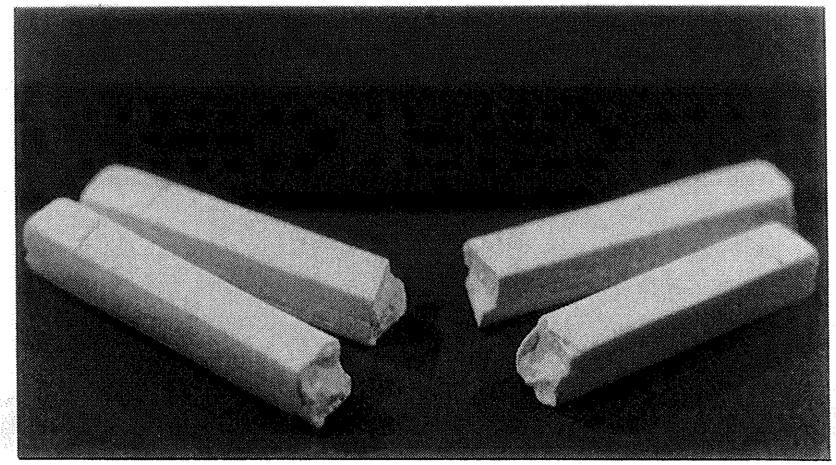

Figure 2 : Fractured fired fused silica MOR bars made by FDC.

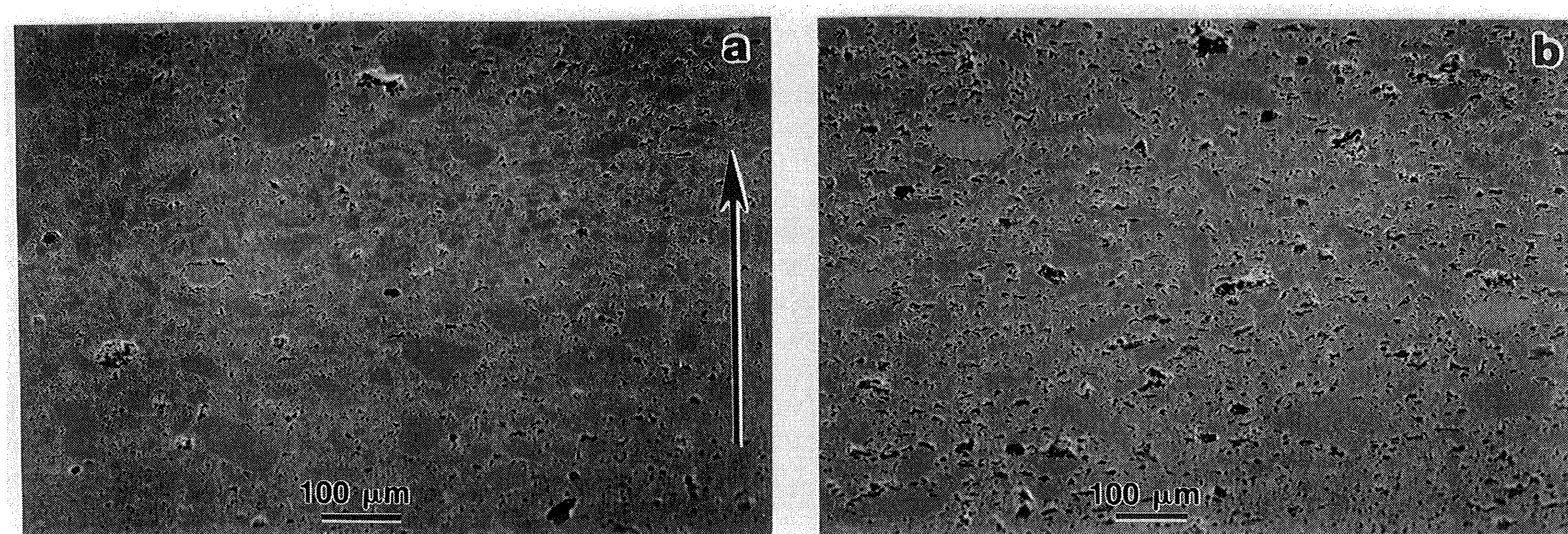

Figure 3: SEM micrograph of a polished cross section of fired fused silica samples processed by (a) FDC (arrow indicates the build direction) and (b) Injection Molding.

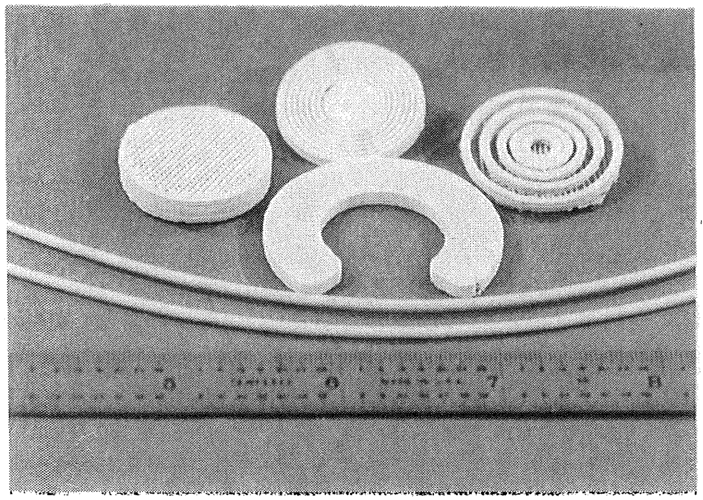

Figure 4: Green PZT filament used for FDC processing and structures and shapes for piezoelectric applications fabricated by FDC processing.

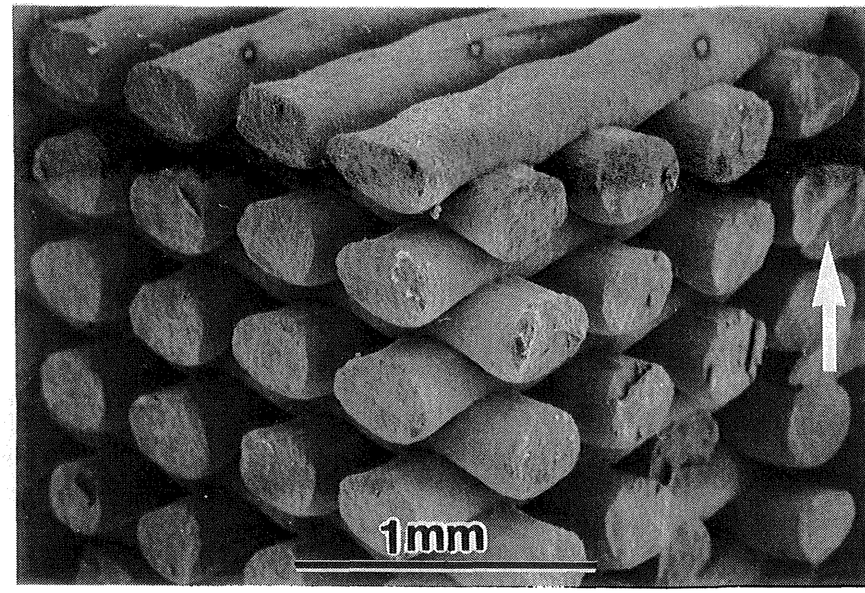

Figure 5: SEM micrograph of a sintered PZT three-dimenisonal ladder structure fabricated by FDC processing (arrow indicates the build direction).

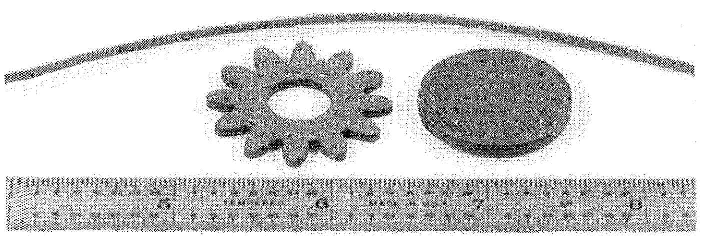

Figure 6: Green stainless steel (17-4PH) filament used for FDMet and parts fabricated by FDMet processing.

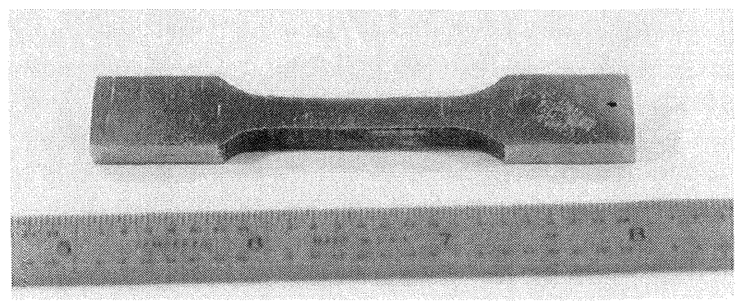

Figure 7: Sintered stainless steel (17-4PH) tensile coupon fabricated by FDMet processing.