Filament Feed Materials for Fused Deposition Processing of Ceramics and Metals

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Fused Deposition of Ceramics (FDC) and Metals (FDMet) are SFF techniques, based on commercial FDM™ technology, for fabrication of ceramic and metal components. The FD processes use feed material in the form of filaments which require certain physical and mechanical properties. FDC and FDMet processes employ filaments formed from ceramic or metal powders mixed with thermoplastic polymers. The thermoplastic polymers act as binder during the FDC and FDMet processing in forming a green part. Development of green ceramic or metal filaments for FDC or FDMet processing involves three critical steps : selection of an appropriate binder chemistry, appropriate mixing procedures and filament fabrication techniques. This study describes the properties required for filaments for successful FD processing and the approach taken in the development of a series of binder which meets these requisite properties for a wide range of ceramics and metals. Appropriate mixing and filament forming techniques are also discussed.

I. Introduction

Most of the SFF techniques for fabrication of ceramic and metal parts employ polymeric binder systems to bond the ceramic or metal particles together in forming a green part [1]. The green part is then processed to remove the binder from the part and then sintered or infiltrated with a lower melting second phase [1]. However, fabrication of green ceramic or metal parts by various SFF techniques have been far from trivial. First, effort is required in developing the proper binder chemistry to allow SFF processing. In addition, effort may be needed in developing suitable dispersants for the specific particulate system and the binder chemistry. Once an appropriate binder chemistry and dispersant have been selected, the ceramic or metal powder systems are processed with the binder and dispersant to form the feedstock in a suitable physical form (powder, sheets, filaments) for specific SFF processing [1].

Each SFF technique requires feedstock materials with certain physical and mechanical properties. Poor selection of binder chemistry, dispersant, and poor processing of the feedstock can lead to unsuccessful SFF processing. This study describes the development of green ceramic and metal filament feedstocks for successful processing by Fused Deposition of Ceramics (FDC) and Metals (FDMet). FDC and FDMet are SFF techniques, based on commercial FDM™ technology, which are being developed for a wide range of ceramics and metals to produce complex shaped ceramic and metal parts with functional properties [2-5]. This study discusses the various physical and mechanical properties required in the filament feedstock for successful FD processing. The study also describes the development of a binder system and the filament fabrication procedures employed for various ceramic and metal systems.

II. Filament Feedstock Characteristics for FD Processing

The commercial FDM™ systems fabricate wax and polymer parts using continuous spooled filaments as the feed material. The filament is fed through a position-controlled heated liquefier head which deposits molten material in precise locations [6,7]. For the filament to be successfully fed into the liquefier and extruded in molten form out of a nozzle, the filament must have certain properties. The filament, which is fed into the liquefier head by a pair of counter-rotating rollers, not only acts as the feed material, but also serves as an efficient piston for extrusion. Therefore, for a certain material viscosity the filament must have sufficient stiffness and

strength for extrusion, or else the filament will buckle or break after passing through the rollers and not be successful in extruding material [5,7]. Hence, necessary, but not sufficient, conditions for successful FD processing are low viscosity and high stiffness. In addition, the material must have good adhesive behavior for bonding between adjacent roads and layers of deposited material [5,7].

Although filaments with low viscosity, high stiffness, and good adhesion characteristics are sufficient to establish FD processing feasibility, for complete process optimization and automation, the filament feedstock must also posses high flexural modulus and flexural strength [5,7]. High flexural modulus and strength are needed to enable continuous spooling of the filaments onto a spool to provide continuous feedstock supply for the FDM™ system. These properties are also necessary to allow continuous un-spooling of the filament from the spool for uninterrupted feeding (without breaking of the filaments) of the liquefier during fabrication.

FDC and FDMet processing, using commercial FDM™ systems, require development of powder/binder filament feedstocks with the above mentioned properties, namely, low viscosity, high stiffness, good adhesion behavior, high flexural modulus and strength. This is done through binder development and selection of dispersant. In addition to these constraints, development of binder(s) and dispersant for FDC or FDMet must also address issues commonly relevant to all green forming techniques. The binder and dispersant have as high a solids loading as possible (>50 volume%), have good dispersion behavior, and must leave no residue after binder removal.

III. Binders for FDC and FDMet

The binders for green forming techniques typically consist of many components; each added for a specific role in the final mix. In this study a four component binder system has been developed for FDC and FDMet processing. As shown in Table I, each of these components plays a specific role in the final formulation. Table I also shows the temperature range at which each of these components volatilize during binder removal. The amount of each component in the formulation used for FDC or FDMet is varied to tailor the properties needed to allow successful FD processing of specific ceramic or metal system. The weight percent of each of these components varied in this study for FDC/FDMet is also shown in Table I. This binder system is designated RUx (x is the identification number of a particular binder formulation under consideration) [5].

The particulate systems studied for FDC and FDMet processing to date include silicon nitride, silica, lead zirconium titanate (PZT), stainless steel, and tungsten carbide-cobalt. Initial feasibility studies for each of these particulate systems were done by using the RU1 binder formulation which contains 30% wax, 35% polymer, 15% tackifier, and 20% elastomer by weight. 50 to 65 volume % powders were mixed the RU1 binder and fabricated into filaments for FD feasibility studies. In addition, viscosity measurements were made on the mixed feedstock. Based on the viscosity behavior and FD feasibility studies, the binder formulation were further optimized. Also, dispersants were selected and used for certain particulate systems to facilitate FD processing. Depending on the study done with each particulate system, the binder formulation development and dispersant selection was either limited to developing filaments which are FD process worthy but not flexible or was developed to produce FD process worthy and continuous and flexible filaments. Table II shows the different RU binder formulations used successfully for FDC and FDMet processing of various materials. The Table also shows the amount of powder used for FD processing of each system and the nature of the filament feedstock thus produced.

Binder and Dispersant Development for FDC of Silicon Nitride

Most significant FD process development to date has been done with Si_3N_4 [3-5]. Although initial FDC trials of 60 volume % Si_3N_4 with RU1 binder formulation were successful, the filaments were rigid and not flexible enough to enable spooling for continuous and automated

FDC processing. To facilitate continuous and automated FDC processing of Si_3N_4, the RU binder was tailored and optimized by a linear Design of Experiments (DoE) [5]. Nine different RU formulations with a wide range of wax. polymer, tackifier, and elastomer contents were used. Viscosity measurements were made on each of these compositions as a function of temperature and shear rate to get the viscosity response as a function of each of the components. Similarly, glass transition temperatures (T_g) were measured for each formulation using Differential Scanning Calorimetry. T_g is commonly used as an indicator of the flexibility of the material. The data from the DoE was analyzed to determine the effects of the various components on flexibility and viscosity. Using a linear representations of the response,

$$\text{Response} = C_0 + C_1\,[\text{tackifier}] + C_2\,[\text{elastomer}] + C_3\,[\text{polymer}] + C_4\,[\text{wax}]$$

the coefficients (C_0 -C_4) for the effect of each component on viscosity and flexibility were calculated [5]. From this linear DoE study, the following conclusions were drawn:

- The tackifier and elastomer improve flexibility and the wax adversely affects the flexibility.
- Elastomer increases the viscosity and the wax lowers the viscosity.

Based on the results of DoE, the binder system RU9 was developed. RU9 formulation contains 20% wax, 19% polymer, 35% tackifier, and 26% elastomer by weight. In addition to developing RU9 binder formulation, a suitable dispersant was also selected. Selection of oleyl alcohol as dispersant was done by a screening process from among several commonly used dispersants for ceramics, especially silicon nitride [5]. The screening of dispersants was done by measuring the viscosity of 30 volume % Si_3N_4 loaded RU binder suspensions. For the dispersant screening experiments, the powder was pre-treated with varying amounts of different dispersants, prior to mixing in RU binder. Based on these screening experiments by measuring viscosity, as shown in Figure 1, 3 weight % oleyl alcohol, which exhibits the greatest decrease in the viscosity, was determined to be a suitable dispersant [5,8]. Hence, the Si_3N_4 powders used in the study were pre-treated with 3 weight % oleyl alcohol, prior to mixing with the RU9 binder formulation. As shown in Figure 2, filaments fabricated from green feedstocks, containing 45% RU9 binder and 55% Si_3N_4 powder by volume, pre-treated with 3 weight % oleyl alcohol, were flexible, continuous and easily wound onto a spool for successful FDC processing. Although the viscosity of Si_3N_4 FDC formulations were considerably higher than that of an FDM™ material, investment casting wax, Figure 3, FDC processing of these materials was equally successful.

Binder Development for FDC and FDMet of Other Materials

As indicated in Table II, binders for other material systems (silica, PZT, stainless steel, and tungsten carbide-cobalt) have not been optimized to result in continuous and flexible filaments. The binders for these materials were developed with appropriate viscosity to allow successful FD processing using small pieces (6"-12" in length) of stiff and rigid filaments, Figure 4. FDC and FDMet processing of 65 volume % silica and 60 volume % stainless steel was feasible with the RU1 binder without the use of any dispersant. However, the RU1 binder was tailored and developed to allow FD processing of PZT and WC-Co. Initial FD analysis of 50 to 55 volume % PZT and WC-Co with RU1 binder indicated viscosity levels much higher than permissible for successful FD processing. Therefore, suitable dispersants have been selected for PZT and WC-Co to lower the viscosity of 50 volume % powder in RU1 binder composition. Figure 5 shows such a lowering of viscosity of 50 volume % WC-Co when pre-treated with 1 weight % dispersant. Use of appropriate dispersants for PZT and WC-Co have enabled successful FD processing with 50 volume% loading in RU1 binder, although the filaments remain rigid. As was done for silicon nitride, it is expected that appropriate dispersant selection and RU binder optimization would result in continuous and flexible FD process worthy filaments for these materials and for other ceramic or metal systems.

IV. Compounding of Ceramic or Metal Powders with Binders

Once the powder, binder and dispersants have been selected for the FDC/FDMet process, the next concern is homogeneous mixing of these ingredients. Mixing or compounding is crucial, since deficiencies in the quality of mixed feedstock can not be corrected by subsequent processing adjustments. Failure to deagglomerate and evenly distribute the powder at this stage will result in downline defects in both FDC fabrication and post-processing operations. Various techniques, such as, measurement of mixing torque or energy, shear modulus, viscosity, etc. are used to assess the quality of mix and to ensure consistent and repeatable compounding from batch to batch.

Both heat and shear are required for efficient compounding of RU-type thermoplastic binders and the ceramic or metal powders. Therefore, torque rheometer mixing was selected as the method for compounding FDC/FDMet feedstocks. Torque rheometer mixing also measures the torque of mixing which is used in assessing the quality of mix. When dry powder is first added to the molten binder, a high torque value is recorded due to entrapment of the binder between and in the powder agglomerates. As the agglomerates break down by the shearing action of the blades, the immobilized entrapped liquid binder is released and hence the torque goes down to a constant level and stabilizes. The stabilized torque is determined by the solids loading, temperature of mixing, speed of mixing, and the dispersing qualities of the binder. Any change in mixer speed (shear rate) and temperature will cause the torque to change since the system viscosity, and hence the torque, are shear rate and temperature dependent.

Experimental Procedure and Results for Compounding:

In this study, the compounding procedure for incorporating ceramic or metal powder into the binder system involves the use of Haake Rheocord torque rheometer [9]. The torque rheometer is fitted with batch mixing bowls of capacities 50 cm^3 and 250 cm^3, with Z-blades to provide shear mixing. The maximum blade speed of the mixers is 150 rpm and the maximum temperature capability is 200°C. The mixing bowls are double walled with three independently heated zones. The middle zone is both air cooled and heated to maintain precise temperature control and prevent overheating due to heat dissipation during shear mixing. The temperature of mixing was determined by the viscosity of the system being compounded. The viscosity of the system being compounded determines the shear stresses generated, which in turn determine how effectively the agglomerates are broken and the particle system is dispersed. However, while generating high shear stresses to effectively break up agglomerates, care was taken not to exceed the torque limits of the mixer. Therefore, the temperature of mixing used for a specific system was dependent on the viscosity of the system. Higher temperatures (100-120°C) were used for systems with high viscosities and lower temperatures (70-90°C) were used for systems with low viscosities [5].

The required amount of binder is weighed and added to the mixer and allowed to melt completely. Once molten, dry powder is added in measured increments of 5-40 grams, depending on the viscosity of the binder system. After each addition, the torque of the system increases instantaneously and then slowly decreases and stabilizes over a period of few minutes. The next incremental amount is added after the steady state torque is reached. The process is continued until a desirable powder loading is achieved, after which mixing is continued for a fixed period of time (1-2 hours). The incremental amount of powder additions is decreased at high volume fractions (>45%). The rotor speed is kept at 100 rpm throughout the process. Figure 6 shows the spikes in torque values for each incremental addition of silicon nitride powder in the RU1 binder and subsequent torque stabilization and the final stabilized torque for one hour of mixing. The quality of mix from batch-to-batch of a particular formulation was constant as indicated by reproducible viscosity measurements made on different batches after compounding [5]. The compounded powder/binder system is removed from the mixer, cooled to room temperature, granulated and sieved to >1mm size for feedstock for subsequent viscosity measurement and filament fabrication.

V. Filament Fabrication

After compounding, the next step in preparing the feed material for FDC or FDMet process is to fabricate filaments of nominal diameter 0.070". The control software for the FDM™ system sets the roller speed, and hence the flow rate, for a given set of build conditions (road width, slice thickness and liquefier head speed) based on the assumption that the feed filaments are 0.070" in diameter. If the filament diameter is less than 0.070" then the flow rate is less than desirable, creating roads with smaller widths and thickness. Such underflow results in poor bonding between adjacent roads and layers or creates voids between adjacent roads and layers. If the filament diameter is much greater than 0.070" then either the filament is not fed into the liquefier, which typically has an opening of 0.073", or it may cause overflow resulting in poor definition of fine features in the part. Therefore, it is important to fabricate filaments for FD processing with very controlled diameter (0.070" ± 0.001"). It is also important that the filaments maintain a circular cross-sectional geometry to be appropriately gripped and fed by the rollers. In dealing with ceramic or metal loaded filaments, it is also important to ensure homogeneous distribution of the binder and particle phases in the filaments with no density gradients and porosity.

In this study, filaments for FDC/FDMet processing were fabricated by two different techniques - capillary extrusion and single screw extrusion. Small quantities of straight, rigid filaments for FD trials were fabricated using an Instron capillary rheometer as a piston extrusion device. The capillary rheometer barrel and plunger are mounted on an Instron mechanical test frame. The barrel was heated to 60°C to 120°C, depending on the material under consideration, and filled with compounded and granulated green ceramic or metal feedstock. Extrusion was done by moving the plunger through the barrel at a constant speed of 1mm/minute. A capillary die of 0.070" was used to produce 6"-12" length segments of the filaments with a diameter of 0.070" ± 0.002". The filaments used in this study for FDC and FDMet processing of SiO_2, PZT, WC-Co, and stainless steel were fabricated using the capillary rheometer approach.

Optimized feedstock formulations, such as 55 volume% silicon nitride (pre-treated with 3% oleyl alcohol) in RU9 binder formulation, were used to fabricate continuous and flexible filaments using a continuous single screw extrusion process. A Haake single screw extruder with a 1" diameter screw and L/D ratio of 20:1 was used [8]. The Haake torque rheometer drive unit, used for compounding feedstock, was used for driving the extruder also [8]. Compounded green feedstock material of particles size in the range of 1.4 mm to 4.0 mm were used as the feed material for extrusion through a die of 0.075" diameter attached to the extruder. Extrusion was done at a screw speed of 10 RPM and the temperature was controlled in four different zones along the length of the screw and barrel. Typically, the temperatures in the feed zone and the die region were kept low at 50°C and 65°C, respectively. The temperatures in the mid-section of the screw length were kept at 75°-100°C. As the filament was extruded, it directly passed onto a moving conveyor. The conveyor speed was adjusted and set to produce controlled drawing of the filaments into final diameter of 0.070" ± 0.002" as it is extruded through a die of 0.075". From the conveyor, the filament passes through an *on-line* diameter measuring device, LaserMike, which continuously records the diameter of the filament. The continuously extruding filament, after passing through the LaserMike, were wound onto spools using an automatic winder. The spools used for winding the filaments are similar to those used in commercial FDM™ systems, shown earlier in Figure 3.

The diameters of filaments fabricated by single screw extrusion as well as capillary extrusion were consistently in the range of 0.070" ± 0.002". Effort is being made to further enhance the diameter uniformity to 0.070" ± 0.0005" by employing pressure control devices, such as a metering pump, in the single screw extrusion process line. The density measurements made on randomly chosen segments of filaments using He pycnometry consistently indicated 100% theoretical density of the mixed feedstock, suggesting no porosity or density gradients along the

lengths of the filaments. As shown in Figure 7, the microstructure of the cross-section of the green filaments exhibited uniform and homogeneous mixing with no phase separation.

VI. Conclusions

This study describes the various physical, thermal, and mechanical properties required in the filament feedstock for successful FDC and FDMet processing of ceramics and metals using commercial FDM™ systems. A unique binder series, designated as RU binders, for FDC and FDMet processing has been developed and successfully applied to a wide range of ceramic and metal systems. It has been shown that through optimization of the RU binder system and appropriate selection of dispersant for a specific particulate system, automated FDC and FDMet processing of many particulate ceramic, metal, and composite system is feasible. Appropriate green feedstock compounding and filament fabrication procedures for FD processing have been established. Green feed filaments with controlled diameter and material homogeneity have been successfully fabricated and used for FDC/FDMet processing.

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TABLE I
Binder Components in the RU Series of Binders

Binder Component	Weight % Range	Component's Role	Thermal Degradation Temperature Range
Polymer	10 -45	Acts as a backbone	100 - 510 °C
Elastomer	30 - 65	Imparts flexibility	275 - 500 °C
Wax	15 - 50	Viscosity modulator	200 - 500 °C
Tackifier	10 - 40	Promotes adhesion	190 - 475 °C

Table II
Binder Systems for FDC and FDMet

Particulate System	Binder System	Vol. % Solids	Dispersant	Filament Fabrication & Quality
Si_3N_4	RU1	60	None	Capillary extruded: Straight & stiff pieces
Si_3N_4	RU9	55	3% Oleyl Alcohol	Single screw extruded: Continuous, flexible, & spooled
SiO_2	RU1	65	None	Capillary extruded: Straight & stiff pieces
PZT	RU1	50	1% Oleyl Alcohol	Capillary extruded: Straight & stiff pieces
WC-Co	RU1	50	1% Oleyl Alcohol	Capillary extruded: Straight & stiff pieces
Stainless Steel	RU1	60	None	Capillary extruded: Straight & stiff pieces

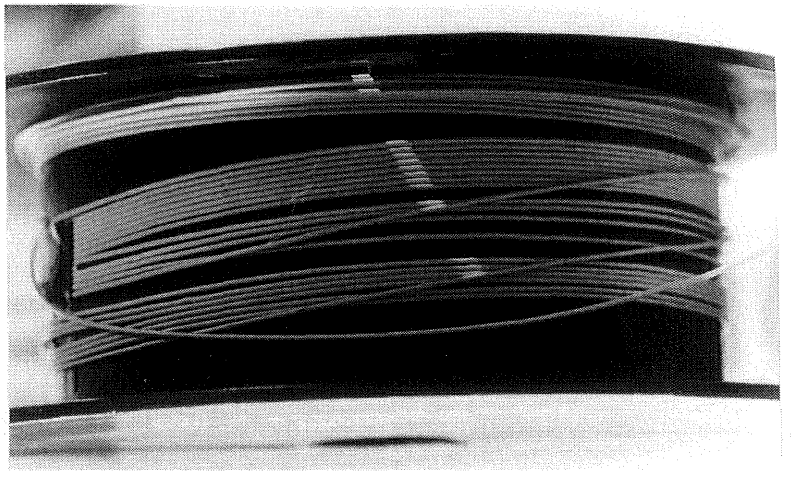

Figure 2: 55 vol.% Si_3N_4 green filaments fabricated using RU9 binder wound on a spool for commercial FDM™ systems.

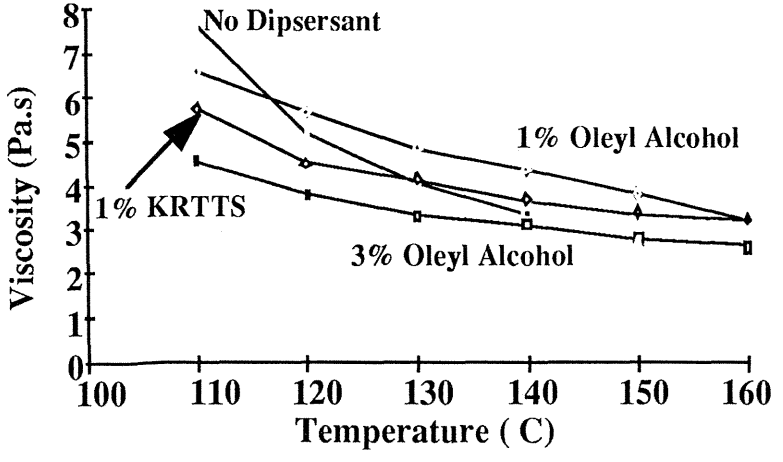

Figure 1: Viscosity as a function of temperature for 30 vol.% Si_3N_4 suspensions in RU1 binder with and without dispersants.

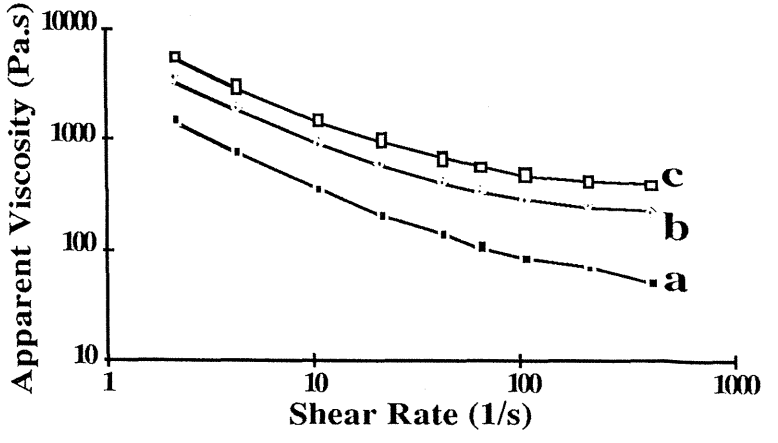

Figure 3: Viscosity vs. shear rate at FD processing temperatures; (a) investment casting wax at 70°C, (b) 55 vol.% Si_3N_4, with 3 wt.% oleyl alcohol, in RU9 binder at 130°C and (c) 60 vol.% Si_3N_4, without dispersant, in RU1 binder at 150°C.

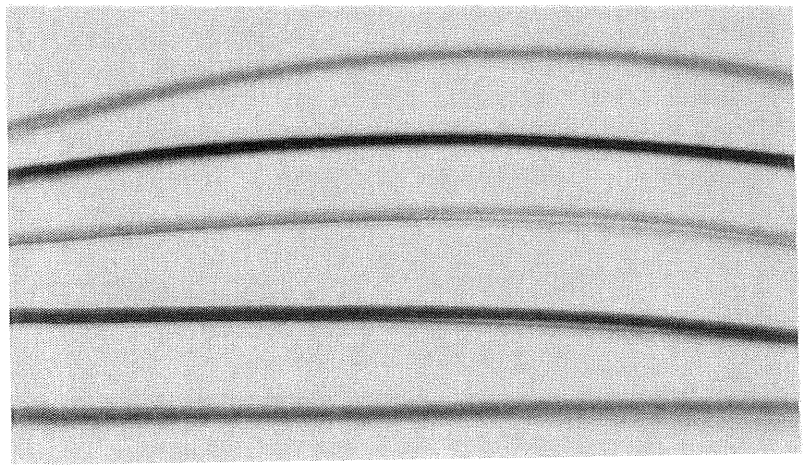

Figure 4: Different ceramic and metal green filaments for FDC and FDMet processing (Top to bottom: Si_3N_4, WC-Co, PZT, stainless steel, andSiO_2).

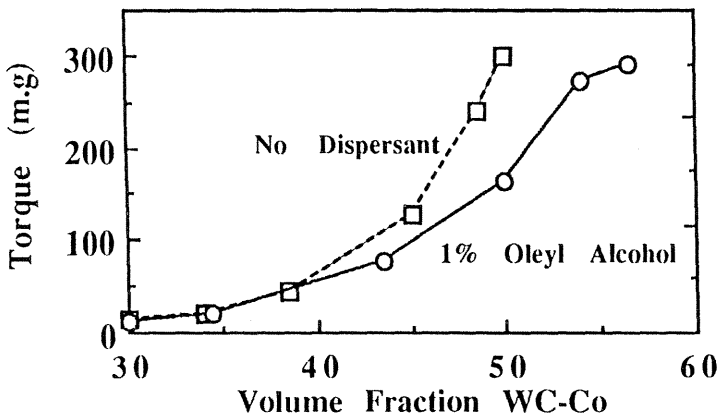

Figure 5: Final steady state compounding torque vs. volume fraction of WC-Co in RU1 binder with and without dispersant indicating a decrease in viscosity with use of dispersant.

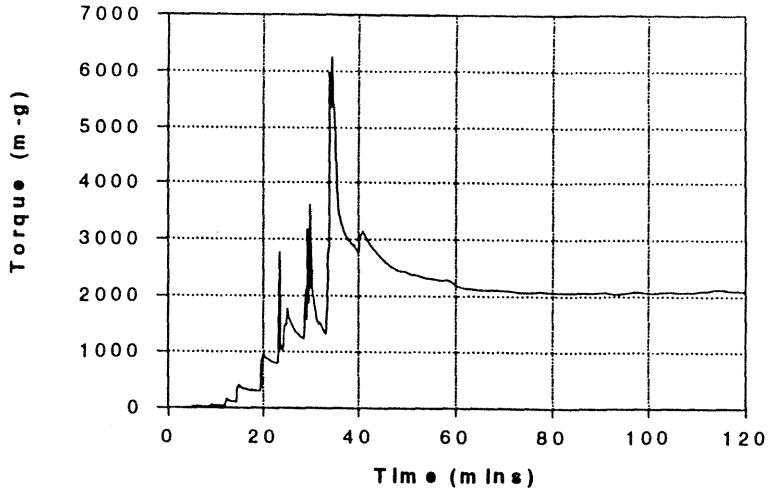

Figure 6: Compounding torque vs. time plot for 60 vol.% Si_3N_4 in RU1 binder using a torque rheometer. The peaks indicate the points of incremental powder additions.

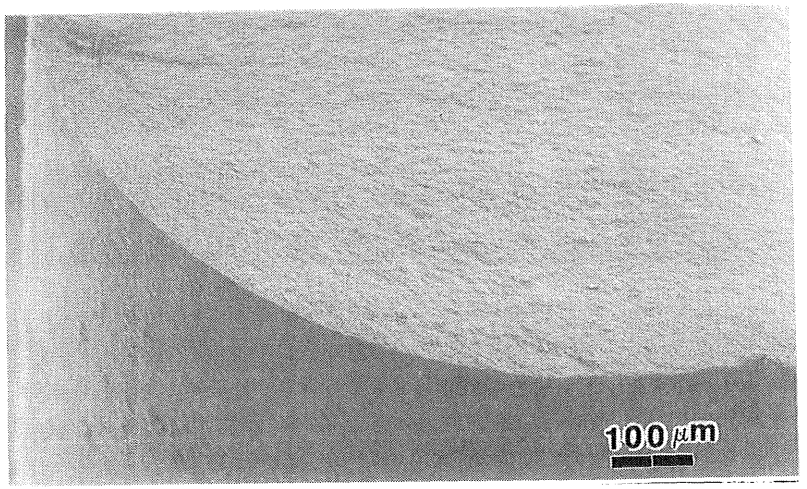

Figure 7: SEM Micrograph of a cross section of green Si_3N_4 filament used for FDC processing.