Performing Supercritical Fluid Extractions With Undergraduates

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ABSTRACT:

Supercritical fluids and in particular supercritical carbon dioxide have shown to be a viable technology for a variety of extractions. While process conditions require high pressures, technological advances have now made it feasible to acquire such equipment for the undergraduate laboratory. One novel application we are currently investigating involves supercritical fluid extraction of organic binders from metal parts produced by powder injection molding (PIM). The initial proof-of-concept studies have been undertaken in our laboratory with bench top equipment manufactured by Supercritical Fluid Technologies, Inc.[a]

OBJECTIVES:

The objective of this proposal is to demonstrate the feasibility of implementing a unique technique of binder removal through Supercritical Fluid Extraction (SFE) of powder injection molding (PIM) fabrication of large volume (> 100 cm^3) components. Supercritical fluid extraction of the binder phase can be accomplished in relatively short process time, while retaining the dimensional control necessary for the production of critical, high-performance components.

In the powder metallurgy (P/M) industry, the removal of the organic “binder” phase from as-injection molded components remains both a production rate limiting issue as well as the major factor influencing the quality of components. The development of binder removal techniques, like the proposed SFE process, to address this limitation has lagged since the overwhelming majority of PIM components produced today are relatively small, with thin structural sections, as seen in Figure 1.

Additional advantages of the proposed SFE de-binding technology are related to the processing of process sensitive nanocrystalline P/M materials. Other materials systems that are not nanostructured would also benefit from this concept including titanium alloys, magnetic materials, and other refractory metal based systems. Long-range objectives of this project include the following.

- De-binding of PIM components larger than 100 cm^3, especially for advanced materials systems such as refractory or nanocrystalline metals.
- A binder removal method that is conducive to producing defect-free components.
- An overall processing system which is economical based on process yield and throughput, capital equipment investment and versatility.
- A binder removal technique which is environmentally friendly.
- A binder removal technique suitable for use with most currently available commercial feedstock and materials systems.

FIGURE 1. TYPICAL PARTS PRODUCED BY POWDER INJECTION MOLDING (PIM)[b]

POWDER INJECTION MOLDING (PIM)

Powder injection molding (PIM) of complex metal or ceramic components combines the shape forming ease of polymer injection molding with traditional ceramic and metal powder processing procedures. By injecting a relatively low viscosity mixture of metal or ceramic powder and organic binder into a mold cavity, complex components can be formed in high production volumes. After removing the binder phase through decomposition or dissolution, the remaining powder compact can be heat treated to final density using well established sintering principles.

Four critical steps in the PIM process include:

- preparation of a suitable powder/binder mixture (i.e. feedstock)
- injection molding of the feedstock into “green" components
- binder removal
- sintering to final density

Injection molding of metal components has been a P/M industry mainstay for over 20 years, yet remains in use primarily for production of relatively small parts (< several cm maximum dimensions) with thin cross sections (< 1 cm). Materials which have been successfully injection molded commercially include iron, steel, stainless steel, Ni based superalloys, tungsten, carbides, magnetic alloys, titanium and others. Typical components include such items as mechanical levers, guides, mounts and fasteners, medical instruments, electronic packages, magnetic motor components, cutting tool inserts, engine components, etc.

While there are numerous de-binding methods, which are suitable for the commercial production of typical PIM components, there are no universally recognized methods for de-binding large volume, precision components.
The purpose of this project is to develop an enhanced SFE method for the extraction of polymer binder materials from large volume PIM components.

It is not the objective of the proposed work to redesign all phases of the PIM process, but simply to replace outmoded de-binding operations with a more efficient and widely applicable technique, supercritical fluid extraction. There is no de-binding approach that is rapid, safe, easily implemented, provides high process yield and is universally applicable to the major feedstock systems which are currently available commercially. The most common techniques are summarized in Table 1.[1] A key approach to reduce the length of the de-binding cycle is to implement multi-component binder systems.

To provide a low viscosity medium for carrying the metal or ceramic powder through out the injection molding forming operation, low molecular weight polymers, waxes and oils are often used as binder components. These materials typically exhibit low melt viscosities, low melting temperatures and are processed more readily and safely by chemical and thermal means than most other organic materials. In concept, the use of at least two binder components in significant proportions allows for the preferential removal of one of the components by selective thermal or chemical means. The initial removal of one of the components, permits the remaining component to remain, providing handling strength and shape retention ability to the remaining powder compact. Often this component, referred to as the “major” component, comprises up to two-thirds of the overall binder. The remaining “minor” or “backbone” binder can then be readily removed prior to high temperature sintering since a relatively open powder/binder structure is developed after the removal of the major binder phase. This 0pen network of porosity allows for the relatively rapid extraction of remaining binder by chemical or thermal means.

In most PIM feedstock systems, the “backbone” binder is a higher molecular weight polymer such as polypropylene, polyethylene, acrylics, acetals or various co-polymers. These materials provide resistance to the removal technique used to extract the major phase, yet can still be readily dissolved or decomposed without contaminating the remaining powder compact with unwanted carbon or oxygen containing by-products.

By applying supercritical fluid extraction (SFE) for PIM debinding, some or all of the organic material can be effectively removed without detrimentally affecting the structure of the remaining powder compact. In addition to numerous process advantages, SFE also has the advantage of being applicable to the many PIM feedstock binder formulations available commercially or being prepared for captive consumption.

De-Binding technique	Features	Advantages	Disadvantages
solvent immersion	solvent dissolves major binder component	no chemical reactions. pore channels opened to facilitate binder removal	hazardous solvents used, environmental concerns, drying required; very slow for fine powder systems
solvent vapor condensation	uses heated vapor of solvent to absorb major binder phase	low temperature process minimizes defects	safety, health and environmental concerns with solvent vapors
catalytic depolymerization	heat component in atmosphere containing depolymerization catalyst	process useful for thin and thick sections with good shape retention	unique hazards associated with special acid catalysts and decomposition products; chemical reactions with high surface area powders and other sensitive materials
thermal decomposition	slowly heated component in flowing gas removes decomposed binder	low cost, one step de-binding/sintering	very slow for thick sections, softening binder allows distortion
wicking	thermal decomposition done in powder bed absorbs binder	fast initial rates, ease of use	part distortion, multiple handling steps, separation of component from powder bed material
supercritical fluid extraction	heat and pressurize fluid above the critical point to dissolve binder	no phase changes and minimized defect formation, scalable for component size and throughput	requires precise temperature and pressure control, not well established for commercial PIM operations

TABLE 1. COMMON PIM DE-BINDING APPROACHES

SUPERCRITICAL FLUID EXTRACTION

When gases are placed under high enough pressure they become liquids. If the gas is heated above a specific temperature, no amount of pressure will cause it to become a liquid. This temperature is called the critical temperature and is unique to a given gas. A gas above its critical temperature (T_c) and critical pressure (P_c) is called a supercritical fluid (Figure 2).[2] This "fluid" now takes on many of the properties of both gases and liquids. It has many of the flow characteristics and the low viscosity of a gas where it can diffuse into matrices much faster than a traditional solvent. However, it also has the superior dissolving and extracting properties of a traditional solvent, therefore allowing the supercritical fluid to dissolve and remove analytes at much elevated rates in comparison to traditional solvent extraction methods. By controlling the density (pressure) and temperature, one can control and tune the selectivity of the supercritical fluid to solvate and remove targeted analytes from matrices. Generally, any industrial process that uses any kind of solvent to clean, dissolve, separate, extract, and react any type of chemical product can lend itself to the application of supercritical fluids as a replacement technology. The most common that are in use today are carbon dioxide and water.

SUPERCRITICAL FLUID TECHNOLGY HISTORY AND APPLICATIONS

The ability of a supercritical fluid to dissolve materials was first reported by Hannay and Hogarth at a meeting of the Royal Society of London in 1879. Even though scientists and engineers have been aware of the enhanced solvating characteristics of supercritical fluids for over 100 years, it is only in the last two decades that SCF solvents have been the focus of active research and development programs. The technical community has devoted a great deal of time and money to the study of supercritical fluids and their properties. Since 1985 supercritical fluid extraction technology has moved into the private sector (Table 2 and Figure 3) from the very small <10 mL extraction vessel size up to true production scale equipment such as the Maxwell House Plant in Houston, TX, which decaffeinates 50 million pounds of coffee per year.

Carbon dioxide, used extensively in the food and perfume industry, is relatively inexpensive, non-flammable, and non-toxic. SFE using CO_2 has shown promise for extraction of low molecular weight organic compounds in the ceramic and P/M forming industries.[4,5,6]

FIGURE 3. A 20-LITER EXTRACTION VESSEL UNIT (SFT, INC.) SCALE UP WORK

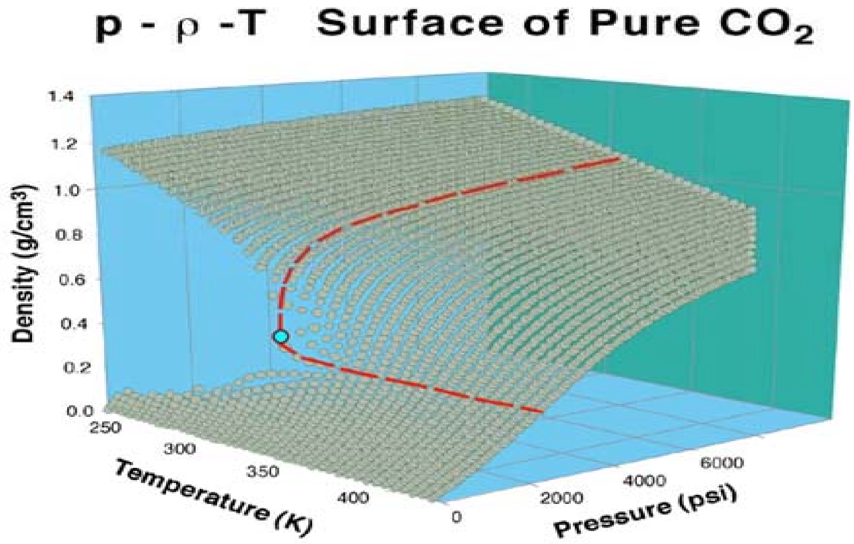

FIGURE 2. CRITICAL PRESSURE/DENSITY/TEMPERATURE OPERATING REGIONS FOR SUPERCRITICAL FLUIDS

Industry	Application
foods and natural products	extraction of fats, flavors, oils and spices extraction of biologically-active molecules environmental testing/pesticide analysis
pharmaceuticals	vitamin and drug purification separating isomers solvent removal synthesis of drugs
polymers	fractionation of specialty polymers preparation of fluoropolymers
textiles	extraction of finishes and dyes determining component mixtures dying and dry cleaning of textiles
aircraft and electronics	cleaning of precision parts and electronics
environmental testing /disposal	extraction of pesticides elimination of chemical weapons soil reclamation

TABLE 2. SUPERCRITICAL FLUID TECHNOLOGY APPLICATIONS

SFE OF PIM BINDERS

Historically, thermal de-binding was the “state-of-the-art” in binder removal where thermal degradation of one or more binder components was removed by complex chemical and physical mechanisms.[3] However, in the last 5-10 years, new binder compositions and novel binder removal methods (Honeywell, Planet Polymer and BASF) have been developed to address the limitations of thermal debinding. However, these approaches are not universal in regard to available feedstock compositions and cannot be integrated into existing production lines without significant process modification. The use of supercritical fluid extraction represents a proven binder removal technique that currently displays great commercial potential based on improved SFE equipment and processes, and the availability of a wide range of feedstock compositions.

The use of SFE for the removal of organic binders from PIM components is based on the dissolution of one or more of the binder components by the supercritical fluid, then diffusion of the dissolved species out through the porous particulate compact. Many complex models exist for describing this process, but will not be elaborated upon here. It is generally agreed among experts in the field of SFE that a typical SCF extraction takes 1/10 the amount of time that a soxelet (liquid/vapor solvent) extraction takes. This would reduce to less than an hour, a typical thermal or solvent debinding process that normally takes several hours or days. The SFE process provides the additional advantage of being a low temperature process (typically < 120°C) , combining temperature with pressure, time and solvent type. The reduction in process temperature whenever possible is critical to the production of components composed of high surface area nanocrystalline metals or other process sensitive materials.

As-molded components are place in the cylindrical pressure vessel, usually on a permeable tray with any necessary supporting fixtures. Carbon dioxide from a storage tank is cooled to –10°C by means of a heat exchanger. The resultant liquid carbon dioxide is pressurized up to the working pressure (> 55 bar) using a pumping system. Then the pressurized liquid is heated up to the working temperature (> 31°C) and pressure (>74 bar), producing supercritical carbon dioxide. The liquid carbon dioxide is introduced in to the pressure vessel, dissolving binder from "green" samples. Both the used carbon dioxide and the extracted binder are captured in a separator, for reclamation and possible reuse. By SFE, as well as with most commercially used liquid solvent de-binding routes, there remains a small fraction of insoluble binder which provides sufficient strength to allow the samples to be prepared for high temperature heat treatment or sintering. Samples which have undergone SFE of the majority of the binder material, can now undergo relatively rapid thermal de-binding since a network of interconnected porosity was opened upon removal of the major binder phase. This open network allows for the rapid percolation of pyrolized species out of the powder compact without fear of damage due to the generation of internal gas pressure. After completion of the binder removal, heat treatment (i.e. sintering) to final density is required, as is the case with all P/M operations.

It is conceptualized that subsequent generations of SFE reactors might also serve provide thermal debinding and sintering services.

An additional advantage of the SFE process compared to liquid solvent extraction is that upon removal from the SFE chamber, the parts are immediately ready for additional thermal processing. The use of liquid solvents requires an additional "drying" step to remove any solvent held in the porous microstructure by capillary action. The additional handling of parts, time to dry, and careful handling of solvent vapors increases the costs associated with producing components by this route.

Many fluids are available for supercritical fluid extraction and reaction including the commonly used carbon dioxide, freon and propane. A comprehensive list of commercially used solvents is shown in Table 3. Many of the other solvents listed are used infrequently due to well documented environmental and safety hazards.

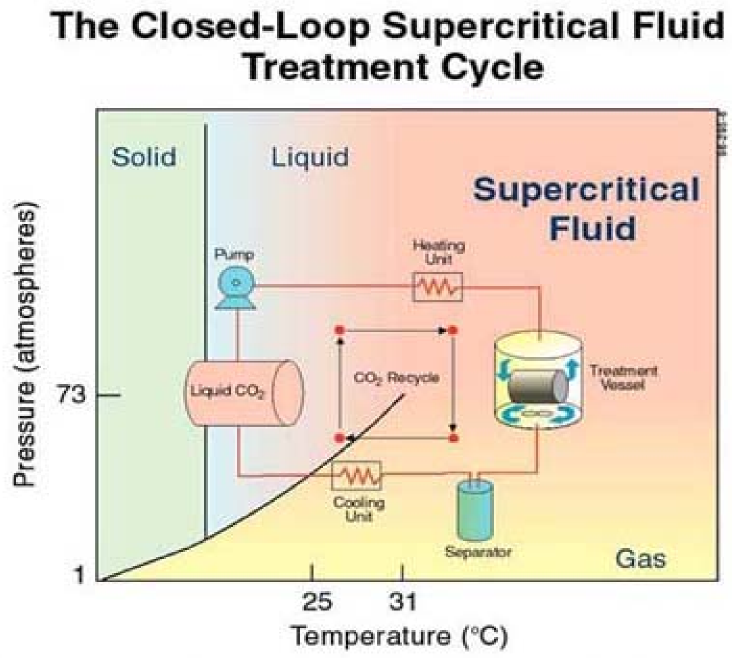

FIGURE 4. SCHEMATIC OF THE APPROACH FOR ORGANIC BINDER REMOVAL VIA SUPERCRITICAL FLUID EXTRACTION

Solvent	**Critical temperature (°C)**	**Critical pressure (bar)**
carbon dioxide	31.1	73.8
ethane	32.2	48.8
ethylene	9.3	50.4
propane	96.7	42.5
propylene	91.9	46.2
cyclohexane	280.3	40.7
isopropanol	235.2	47.6
benzene	289.0	48.9
toluene	318.6	41.1
p-xylene	343.1	35.2
chlorotrifluoromethane	28.9	39.2
trichlorofluoromethane	198.1	44.1
ammonia	132.5	112.8
water	374.2	220.5

TABLE 3. COMMONLY USED SFE SOLVENTS AND CRITICAL TEMPERATURE/PRESSURE CHARACTERISTICS

PRELIMINARY RESULTS:

Small representative PIM samples (3/8" x 3" x 1/4") have been “de-bindered” using supercritical CO_2. As-injection molded samples, containing stainless steel powder in a paraffin wax/polypropylene binder at 65 volume % solids loading, were de-bindered in pure supercritical CO_2. Total binder content was 5.85 wt.%, with the CO_2 extractable component, paraffin wax, at 3.8 wt. % of the total part. After supercritical debinding in CO_2, a weight loss of up to 2.96 wt.% was measured after several trials. This corresponds to over 75% of the available paraffin wax being removed without benefit of optimized extraction conditions or materials. The sample was intact with no signs of distortion or defects.

Trial	Pressure (bar)	Temperature (°C)	% weight loss
1	300	60	2.36
2	400	75	2.95
3	500	100	2.81

TABLE 4. SUMMARY OF SFE TRIALS USING A PIM SAMPLE COMPOSED OF STAINLESS STEEL IN A PARAFFIN WAX/POLYPROPYLENE BINDER

FURTHER WORK: EVALUATION OF SFE FOR COMMERCIAL FEEDSTOCKS

- Viability of this work demonstrated as-molded components fabricated will be de-bindered using SFE. Process conditions will be varied to optimize binder removal rates while preserving the structural integrity and dimensional control of the components. Samples will be analyzed for binder removal performance and microstructural soundness after sintering.

- Modification of process and equipment for large volume components using selected binder systems. Preliminary work has been performed in a 50 mL vessel on a benchtop instrument manufactured by SFT, Inc.

- In this task, an existing large volume SFE system (20-liter unit, Figure 3) will be used to establish procedures to remove target binder constituents in large volume components (thick sections and large planar geometries).

- An eventual closed-loop supercritical fluid treatment cycle is envisioned as follows (Figure 4). The supercritical fluid enters the treatment vessel and into contact with the binder. During this time binder is extracted from the metal part and solubilized in the CO_2. There is a constant flow of CO_2 through the treatment vessel, so that clean, dry CO_2 is continuously made available. On exiting the treatment vessel, the supercritical CO_2, containing the dissolved binder is sent to a separator, where the CO_2 is de-pressurized to below P_c, reducing the CO_2 back to a gas. The solubility of the binder is greatly reduced in the low-density gas phase and is deposited in the bottom of the separator. The clean, dry CO_2 gas exits the top of the separator, where it is liquified by a cooling unit before re-entering the liquid storage unit.

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