

BENCH-SCALE SYNTHESIS OF NANOSCALE MATERIALS

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ABSTRACT

A novel flow-through hydrothermal method used to synthesize nanoscale powders is introduced by Pacific Northwest Laboratory. The process, Rapid Thermal Decomposition of precursors in Solution (RTDS), uniquely combines high-pressure and high-temperature conditions to rapidly form nanoscale particles. The RTDS process was initially demonstrated on a laboratory scale and was subsequently scaled up to accommodate production rates attractive to industry. The process is able to produce a wide variety of metal oxides and oxyhydroxides. The powders are characterized by scanning and transmission electron microscopic methods, surface-area measurements, and X-ray diffraction. Typical crystallite sizes are less than 20 nanometers, with BET surface areas ranging from 100 to 400 m²/g. A description of the RTDS process is presented along with powder characterization results. In addition, data on the sintering of nanoscale ZrO₂ produced by RTDS are included.

INTRODUCTION

Industrial demand for advanced materials has motivated the development of new methods to produce ultrafine powders. Ultrafine powders, also known as nanocrystalline or nanoscale powders, are defined here as those having crystallite sizes of the order of 1 to 100 nanometers. These powders can be used as feedstocks to fabricate materials such as cost-effective catalysts, high-performance components for aerospace and power generation applications, and lightweight/high-strength automotive materials. Ultrafine powders offer distinct advantages over more common microcrystalline powders because they provide high grain boundary area and/or high specific surface area. Unfortunately, common synthesis methods to produce nanoscale powders do not provide production rates sufficient to accommodate industrial needs. In this paper, we describe a hydrothermal process developed at Pacific Northwest Laboratory (PNL) that economically produces nanocrystalline oxide and oxyhydroxide powders at high rates suitable for industrial applications. The process is called Rapid Thermal Decomposition of precursors in Solution (RTDS).

Powders produced by the RTDS process are making an impact in many industries, an important example is in the field of heterogeneous catalysis. Often, the cost of bulk catalyst material may be high, but for ultrafine material having a high specific surface area, the cost per active surface site is very low. This reduces both capital and operating costs. As will be shown in this paper, the

flexibility of the RTDS process allows the powder to be used as catalyst material and as precursors for the fabrication of advanced materials. In the latter application, RTDS powders offer the ability to control the microstructure of a consolidated advanced material which enhances certain mechanical properties.

POWDER SYNTHESIS

Several existing synthesis methods can produce nanoscale powders. Some of the more common nanocrystalline powder synthesis methods are gas-phase condensation, sol-gel processing, and combustion synthesis (1). However, all of these processes have limitations for industrial applications, in particular, low production rate of the powder product. These methods are briefly summarized below.

Gas-phase condensation was first suggested by Gleiter (2) and uses an ultrahigh vacuum system fitted with a heating assembly and a liquid-nitrogen-filled cold finger. Unfortunately, the gas phase condensation process is inherently a batch operation and the production rates are low for industrial standards. Although this process is not yet generally useful in industrial applications, it has enabled researchers to demonstrate the improved room-temperature mechanical properties of nanoscale materials relative to their coarse-grained counterparts (3-5).

Sol-gel technology is a chemical method used to produce oxide material, including ultrafine powders, at room temperature. However, relatively pure precursors for industrially important materials such as nickel, iron, chromium, and zinc oxide are either very expensive or must be synthesized in-house prior to sol-gel processing. In addition, many of the precursors are moisture sensitive, making them difficult to store and handle.

Combustion synthesis combines soluble metal salts and a complexant/fuel such as carboxylate azides, urea, or glycine (6-10). The mixture is heated, and an autoignition reaction occurs which produces the desired powder. This technique is useful for the production of ceramic powders with specific stoichiometry and also for multicomponent systems. However, the technique does not easily yield hydroxides, and the distribution of grain-sizes is large. Also, the powders produced by this method are highly aggregated into hard clusters or agglomerates.

RTDS is a new, flow-through hydrothermal process with the capability to continuously produce nanocrystalline powders at rates of pounds per day using a bench-scale apparatus (11). The RTDS process was recently recognized for its innovative contribution to powder synthesis by receiving the prestigious R&D 100 award for 1993 (12). The process offers a flexibility to control the crystallite size and uniformity while producing powders at high rates.

RAPID THERMAL DECOMPOSITION OF PRECURSORS IN SOLUTION

Process Description

The synthesis of RTDS nanoscale powders begins with a feedstock solution of a metal salt or mixture of metal salts dissolved in water. The bench-scale system primarily consists of a high-pressure pump, a heated region, and a pressure reduction nozzle. The liquid feedstock is pressurized by a reciprocating piston pump and heated to reaction temperature by a standard-tube furnace. Within the heated region, hydrothermal (forced hydrolysis) reactions occur that produce solid oxide and oxyhydroxide particulates. Typical RTDS operating conditions include pressures ranging from 5000 to 8000 psi and temperatures from 200°C to 400°C. After the particles are formed in the heated region, the resulting suspension passes through a pressure reduction orifice. The solid/liquid aqueous suspension is then either used in slurry-based processes or the particulates are separated and dried by standard industrial methods (sedimentation, centrifugation, spray drying, etc.). The RTDS process is shown schematically in Figure 1. Although the present

RTDS system is a bench-scale apparatus, the technology uses standard unit operations which can readily be incorporated into existing industrial facilities.

A key feature of the RTDS process is that the nuclei are formed quickly and are allowed very little time to grow in the hydrothermal region. Typical residence time of the solutions in the heated region ranges from 2 to 30 seconds. This variable can be controlled by either changing the length of tubing within the heated region or varying the flow rate. As a result of the short residence time, crystallite sizes produced by this method are limited to the nanometer range. The particles produced are typically aggregates of nanometer-sized crystallites and are of the order of 100 nanometers. Some control over crystallite size can be exercised by adjusting the residence time of solution in the heated zone.

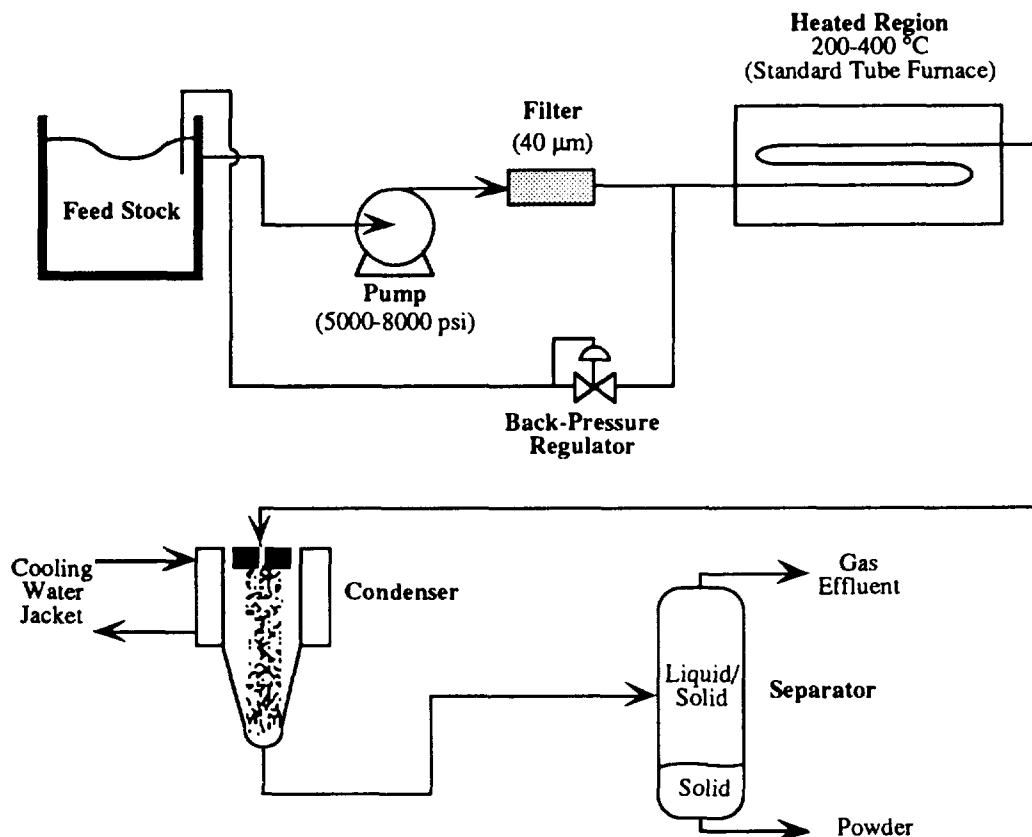


Figure 1. Schematic diagram of the RTDS process.

Powder Characterization

The RTDS powders have been characterized by several techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Brunauer-Emmett-Teller (BET) nitrogen adsorption analysis. The XRD measurements, which allow phase identification and provide crystallite size information, were obtained using a Philips 3000 series X-ray diffractometer with a copper source operated at 40 kV and 45 mA. SEM was performed on an ElectroScan MEM-20 multi-environmental electron microscope. Both bright-field and dark-field TEM micrographs were obtained using a Philips EM400T electron microscope with a 120 keV electron beam. The BET surface area measurements were performed on a Micromeritics ASAP 2000 using multipoint analysis. Some of the powders produced using the RTDS method

and the corresponding crystallite sizes (determined by XRD line broadening analysis) are shown in Table 1.

Table 1. Typical powders produced by the RTDS process.

Material	Chemical Formula	Crystallite size (nm)
Ferrihydrite	5Fe ₂ O ₃ ·9H ₂ O	<10
Hematite	α-Fe ₂ O ₃	23
Magnetite	Fe ₃ O ₄	12
Tenorite	CuO	20
Trevorite	NiFe ₂ O ₃	<10
Bunsenite	NiO	12
Zirconia	ZrO ₂	<10
Zincite	ZnO	34
Anatase	TiO ₂	<10

Figure 2 shows a composite bright-field TEM micrograph of iron oxyhydroxide/oxide powders produced at three different RTDS processing temperatures from an iron nitrate solution. This figure clearly illustrates that RTDS operating conditions affect the characteristics of the resulting powders. In this example, both crystallite size and phase were affected by changes in the RTDS processing temperature. These observations are confirmed by analysis of the XRD patterns for these three materials (Figure 3). The XRD patterns show peak width broadening with decreasing temperature, which indicates a reduction in crystallite size. The XRD measurements were also used to identify the phases present. The predominant phase at the lower RTDS processing temperature (200°C) was 6-line ferrihydrite, while at high temperatures (greater than 350°C) the predominant phase was hematite. A mixture of these two phases was produced at intermediate temperatures.

The BET surface-area measurements of RTDS powders typically range from 100 to 400 m²/g. For example, the 6-line ferrihydrite shown in Figure 2 has a specific surface area of 280 m²/g. Other high surface area RTDS powders of industrial importance include: zirconia = 428 m²/g, anatase = 136 m²/g, and hematite = 153 m²/g.

Suspensions of nanocrystalline materials produced by RTDS provide unique feedstocks for spray drying. Using this method, micrometer-scale spherical aggregates of nanocrystallites are readily produced. Figure 4 shows a SEM micrograph of a ZrO₂ powder produced by spray drying a RTDS-generated suspension of ZrO₂. The drying process yielded solid-core spherical aggregates in the 0.5-μm to 5-μm size range. The morphology of the spray-dried powder is ideally suited for subsequent consolidation processes, such as powder injection molding, isostatic compaction, or hot pressing.

POTENTIAL COMMERCIAL APPLICATIONS FOR RTDS POWDERS

Catalysts

The RTDS powders are an attractive option for heterogeneous catalysts because of their high degree of crystallinity and high specific surface areas. RTDS powders typically do not need to undergo pretreatment steps (such as increasing the number of acidic sites) before becoming

RTDS Powders Produced from 0.1M Fe(NO₃)₃ Solutions

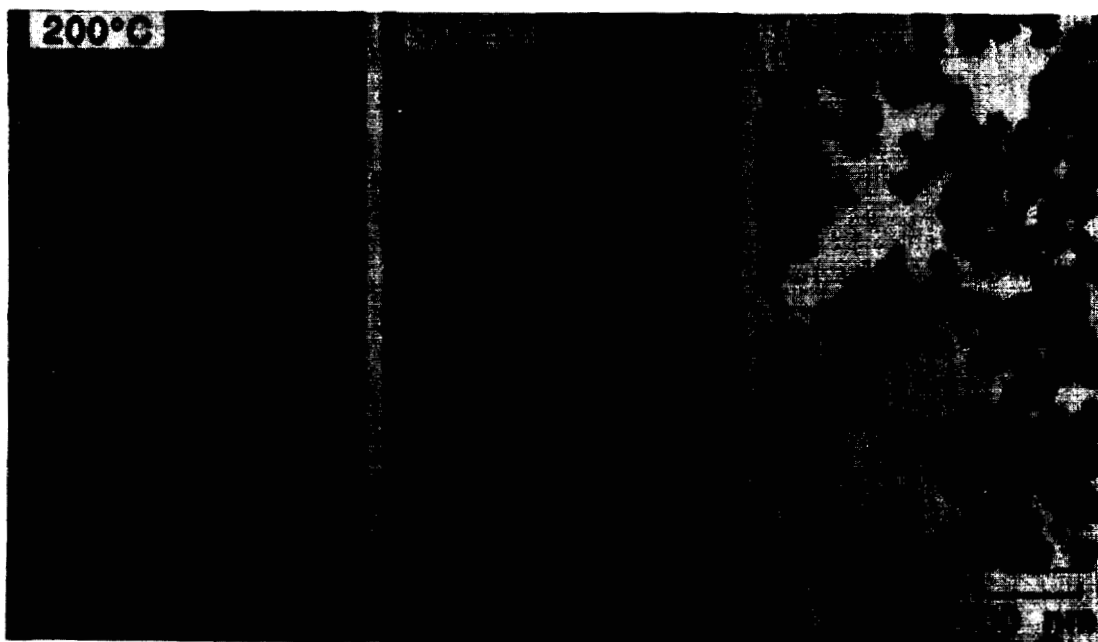


Figure 2. TEM micrographs of RTDS powders produced from iron nitrate solutions at 200°C, 300°C, and 350°C.

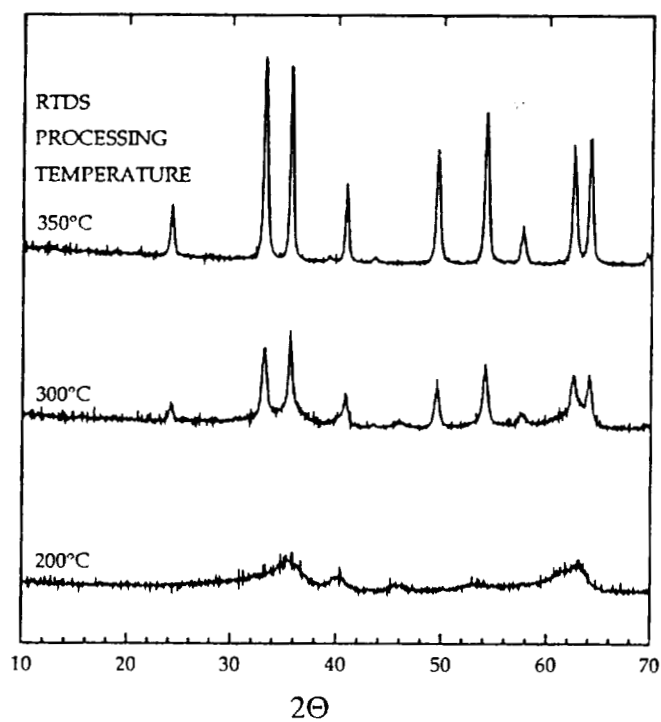


Figure 3. The corresponding XRD patterns for the RTDS powders shown in Figure 2.

"activated" catalysts. For many applications, the RTDS production conditions can be tailored to simultaneously synthesize and pretreat the catalyst powder so that the powder is "preactivated" when collected. RTDS powders can also be consolidated and sintered into porous, high surface area supports for catalysts, or catalyst and support material precursors can be co-processed in the RTDS apparatus to yield a pre-formed supported catalyst.

RTDS powders and supports were tested by workers at PNL and by their industrial clients. Nanoscale RTDS ferrihydrite powder, similar to that shown in Figure 2, was used as a coal liquefaction catalyst, and the activity of the RTDS produced powders was compared with other commercially available catalysts. The RTDS material yielded more liquefied products than any of the other iron-based catalyst tested.

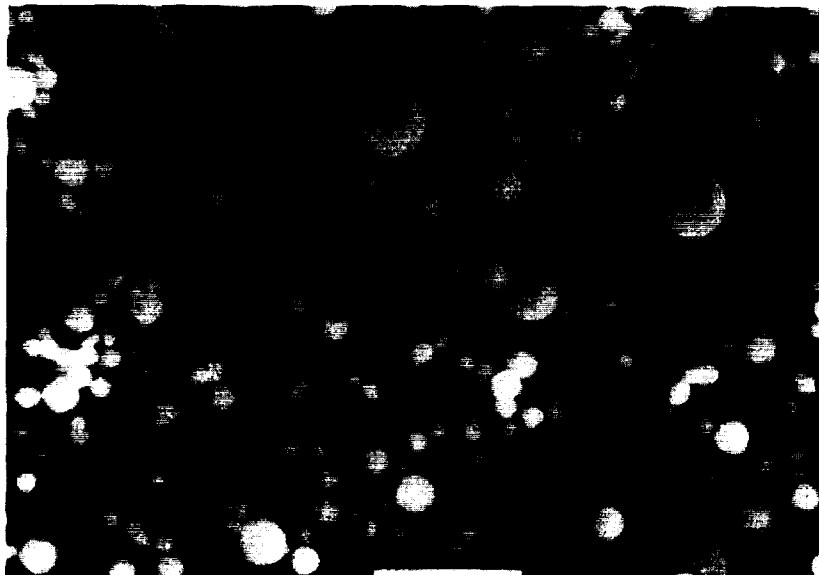


Figure 4. SEM of a spray-dried ZrO_2 powder produced using a ZrO_2 suspension generated by RTDS processing of a zirconyl nitrate solution at $300^\circ C$.

Powder Manufacturing of Components

The properties of nanoscale powders are dominated by their small crystallite size and high interfacial area (i.e., high grain boundary area and/or high surface per unit mass). Therefore, the interfacial mechanism of mass transport under certain processing conditions will control the microstructure of a component produced from a powder precursor. The ability to control the microstructure of the bulk product is advantageous because the physical properties of the material are dependent on the grain size and microstructure of the bulk material. Consequently, nanocrystalline powders provide a unique opportunity to control the microstructure of a fabricated component.

Interfacial phenomena are important when powders are fabricated into bulk materials by consolidation and sintering (13). In conventional powder processing, powders are consolidated into a desired component geometry under high pressure. Subsequently, the component is heated at high temperature (sintered) to produce a part with little porosity. The sintering kinetics for a nanocrystalline powder compact are dominated by grain boundary diffusion because of the extremely high grain boundary areas. In contrast, for microcrystalline powder compacts, volume diffusion typically dominates the sintering kinetics. The activation energy for grain boundary diffusion is lower than that of volume diffusion for nanoscale compacts. Therefore, the lower

activation energy provides nanocrystalline powder compacts with lower sintering temperatures as compared with conventional microcrystalline powder compacts. This fundamental difference in the sintering mechanism also provides an alternative pathway to control the microstructure of the bulk monolith.

The importance of microstructural control in materials is demonstrated by examining the relationship between the mechanical properties of a material and its microstructure. The yield strength and the fracture strength of a polycrystalline material are related to grain diameters in the bulk material by similar expressions:

$$\text{Strength} = K_1 + \frac{K_2}{d^{1/2}} \quad [1]$$

where K_1 is a materials-related constant, K_2 is a collection of appropriate constants, and d is the grain diameter (14). Clearly, smaller grain size improves the strength of such materials.

Creep deformation, or time-dependent strain under an applied stress, is also related to grain size in the bulk material by the relation:

$$\text{Creep Rate} \propto \frac{1}{T d^3} \quad [2]$$

where T is the temperature (15). From Equation 2, the smaller the grain diameter of the material, the lower temperature is required to provide a given creep rate. This is important for nanocrystalline material because creep deformation occurs at lower temperatures, and, therefore, grain boundary rearrangement occurs without grain growth. Also, superplastic forming of nanocrystalline bulk materials becomes more feasible as grain size is decreased (15).

RTDS nanoscale powders can be consolidated and sintered into useful components, often with unique properties. Researchers at PNL and their clients are currently investigating the agglomeration, consolidation, and sintering behaviors of a variety of single and multi-phase RTDS powders. Figure 5 is a plot of relative sintered density as a function of normalized temperature showing two regions: one for nanocrystalline zirconia and the other for microcrystalline zirconia (16). Region I defines an area where 10 nanometer crystallite microstructure will sinter under typical conditions. Region II describes a similar area for 200 nanometer crystallites, which is typical of many conventional microcrystalline oxide systems. Figure 5 also shows sintering characteristics of zirconia produced by the RTDS process.

The RTDS zirconia sintering data fall well within Region I and densifies at lower normalized temperature than the microcrystalline counterpart. The reduction in sintering temperature for the RTDS powder is due to the difference in mass-transport mechanisms and activation barriers associated with each microstructure grain size. Darab *et al.* (13) have shown that the mechanism of sintering for nanocrystalline RTDS zirconia is grain boundary diffusion with an activation barrier of 250 kJ/mol, whereas that of microcrystalline powders is volume diffusion with an activation barrier of 430 kJ/mol. The lower sintering temperatures associated with nanoscale powders can provide significant energy savings when used as a feedstock for powder manufacturing processes.

SUMMARY

The RTDS process enables the production of nanoscale, crystalline oxide/oxyhydroxide powders at industrial-scale rates. The flexibility of the process allows control over the crystalline size and phase. Other synthesis methods are limited by low production rates, and RTDS fills an existing gap in industrial powder production. The powders produced by RTDS have been shown to be

effective catalysts for coal liquefaction and provide lower sintering temperature for zirconia compacts. The bench-scale apparatus is easily scaled to pilot-scale level because the process uses standard industrial unit operations. It is anticipated that the RTDS process will produce unique advanced materials for numerous applications, such as: 1) powders for pigments, magnetic media, and abrasives; 2) additives for advanced composites; and 3) starting materials for the preparation of separation media such as nanoporous filters.

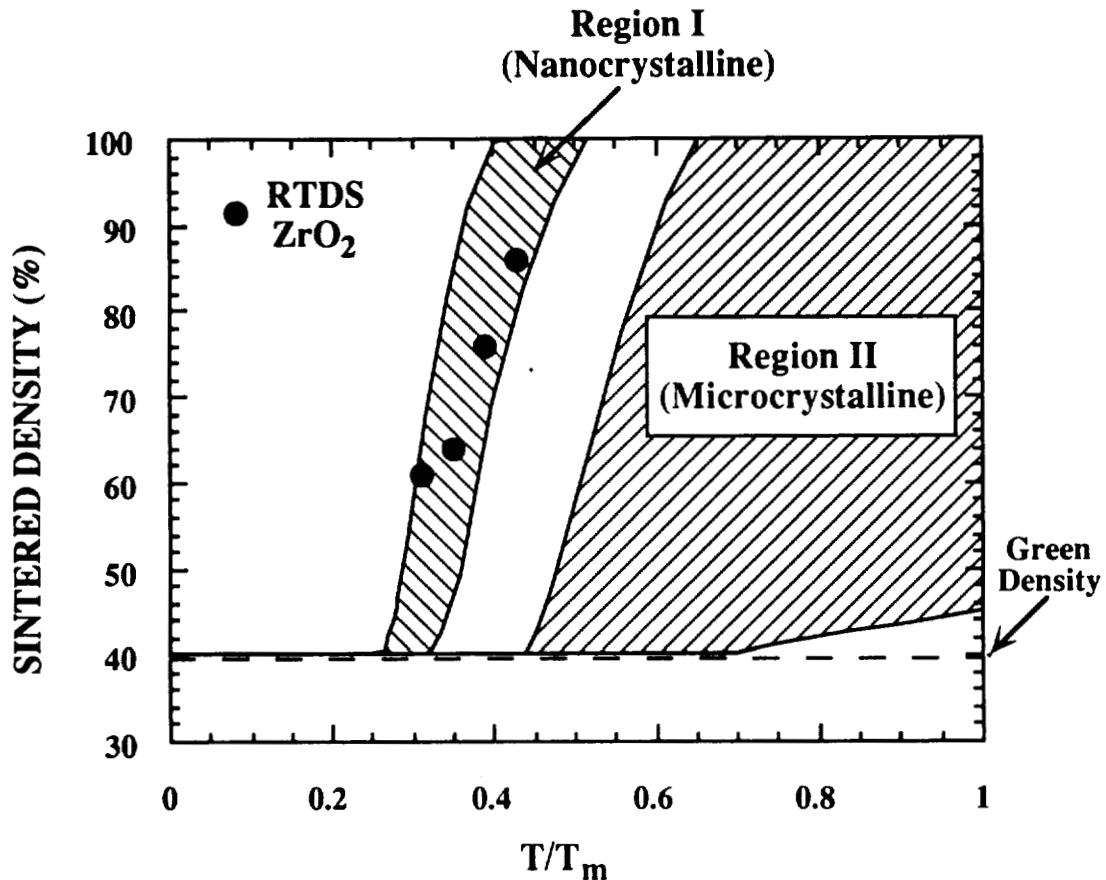


Figure 5. Relative sintered density as a function of normalized temperature ($T_m = 2570^\circ\text{C}$) for nanocrystalline RTDS ZrO_2 and theoretical behavior.

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