W-31-109-ENG-38

Jeffrey A. Eastman
Kurt E. Sickafus
Joel D. Katz

MICROWAVE SINTERING OF
NANOPHASE CERAMICS WITHOUT
CONCOMITANT GRAIN GROWTH

685,117

Title: MICROWAVE SINTERING OF NANOPHASE CERAMICS WITHOUT CONCOMITANT GRAIN GROWTH

Inventors: Jeffrey A. Eastman, Kurt E. Sickafus and Joel D. Katz

MASTER

CONTRACTUAL ORIGIN OF THE INVENTION

The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the U.S. Department of Energy and The University of Chicago representing Argonne National Laboratory.

Background Of The Invention

This invention relates to methods of sintering nanophase materials and more particularly to sintering nanocrystalline ceramics in order to increase densities while retaining small grain size. Ceramics find many uses in industry particularly for electrical components. However, internal flaws and high temperature processing along with negligible ductility of ceramics are problems which mitigate against their uses. Improved physical characteristics have been achieved by reducing the particle size of the starting powders from which the ultimate ceramics are made. Small particle sizes have the advantages that densification depends inversely on the fourth power of particle size, internal flaws associated with larger pores are minimized, and ductility can be gained through other mechanisms known in the art. Ultra fine grain metals have

been prepared by Geitler about 10 years ago, <u>Deformation of</u>

<u>Polycrystals</u>: Mechanisms and Microstructures, N. Hansen et

al. eds (Riso National Laboratory, Roslalde, Norway 1981),

in which inert gas condensation of metal vapors is combined

with in situ collection and compaction of the ceramic

powders to produce nanocrystalline ceramics. These ceramics

have potentially important properties such as low sintering

temperatures and superplasticity. By nanocrystalline

materials, it is meant in this application, materials having

average grain sizes of 100 nanometers or less and preferably

grain sizes of 60 nanometers or less. Green body density of

ceramic nanocrystalline materials can approach 75% of

theoretical, but for most purposes densities of the fired

ceramic should be greater than about 90% of theoretical.

The invention consists of certain novel features and a

combination of parts hereinafter fully described,

illustrated in the accompanying drawings, and particularly

pointed out in the appended claims, it being understood that

various changes in the details may be made without departing

from the spirit, or sacrificing any of the advantages of the

present invention.

Brief Description of the Drawings

For the purpose of facilitating an understanding of the

invention, there is illustrated in the accompanying drawings

a preferred embodiment thereof, from an inspection of which,

when considered in connection with the following

description, the invention, its construction and operation,

and many of its advantages should be readily understood and appreciated.

Figure 1 is a graph showing the time-temperature curves for each of the microwave samples.

Fig. 2 is a graph showing the relationship between grain size and density versus maximum sintering temperature for microwave sintered samples, and

Fig. 3 is a graph showing the grain size versus density plot showing a comparison between the microwave sintering of the invention with prior art nanocrystalline sintering.

Objects Of The Invention

An object of this invention is to provide a method of sintering and densifying nanocrystalline ceramics to provide densities in excess of 90% of theoretical while maintaining grain sizes at 60 nanometers or less.

Another object of the invention is to provide a method of sintering nanocrystalline material comprising subjecting nanocrystalline material to microwave energy to heat the material to a temperature less than about 70% of the melting point of the nanocrystalline material expressed in degrees K, to produce sintered nanocrystalline material having a density greater than about 95% of theoretical and an average grain size not more than about 3 times the average grain size of the nanocrystalline material before sintering.

Another object of the invention is to provide a method of sintering nanocrystalline material comprising subjecting the material to microwave energy sufficient to heat the

nanocrystalline material to a temperature at which the nanocrystalline material both sinters and densifies for a period of time required to obtain a density greater than about 90% of theoretical with average grain size not greater than about 60 nanometers and thereafter cooling said material.

A final object of the invention is to provide a method of sintering nanocrystalline rutile TiO_2 comprising subjecting the rutile TiO_2 to 2.45GH_z microwave energy for a period of time sufficient to raise the temperature thereof not in excess of about 70% of the melting point of rutile TiO_2 expressed in degrees K, thereafter cooling said TiO_2 whereby in excess of 90% of theoretical density is achieved with grain sizes less than about 40 nanometers.

Preferred Embodiment of The Invention

Nanocrystalline materials may be made from a variety of metals and non-metals. Nanocrystalline ceramics have significant uses for both structural and electrical components. Ceramics which are of most interest are the oxides and the nitrides. The term "ceramics" as used herein includes composites of several discrete ceramic phases intermixed as well as ceramic alloys in which a new phase is produced. Some of the ceramics of interest may be formed from one or more of Ti, Mg, Zn, Al, Pb, Cu, Dy, Eu, Pd, Fe, Si, W and alloys thereof either as oxides or as nitrides where applicable. For instance, a ceramic alloy of nanocrystalline W-Mg oxide has been made.

Further, it has been found including dopant quantities
of materials (generally less than about 1 atom percent) in
ceramics may enhance the densification characteristics such
as doping rutile titanium dioxide with yttrium.

One of the inherent problems in densifying bulk
nanocrystalline material while limiting the grain growth
during the densification process is that both densification
and grain growth result from atomic motion, and it has been
difficult to prepare nanocrystalline material having high

10 theoretical densities and very small grain sizes. As used
herein, grain sizes refer to average grain sizes because it
is understood by those skilled in this art that individual
grains larger than nano size may occur while the average
grain size of material will be well within the
nanocrystalline range. Nanocrystalline range as used herein
means average grain size of about 100 nanometers or less and
preferably 60 nanometers or less, it being understood that
in general the smaller the average grain size, the better
the resulting physical characteristics.

20 The rutile phase of nanocrystalline TiO_2 has been
prepared and used extensively in experiments defining the
characteristics of nanocrystalline materials. In addition,
nanocrystalline magnesium oxide has been prepared and these
two oxides illustrate the fact that each ceramic has its own
typical grain size which occurs during the preparation of
nanocrystalline material. For instance, rutile phase
nanocrystalline TiO_2 when prepared as hereinafter set forth

typically has an average grain size of about 12 nanometers
whereas nanocrystalline magnesium oxide when prepared
according to the method hereinafter set forth typically has
an average grain size of about 5 nanometers. Resultant
grain growth during densification starts from the grain size
of the green nanocrystalline material.

It has been found that subjecting the green
nanocrystalline ceramics to microwave energy for a time
sufficient to elevate the temperature of the specimen to
10   between about 60% to about 70% of the melting point of the
material, expressed in degrees Kelvin, results in
densifications between about 90% and 95% of theoretical and
with a resultant increase in grain size from about 1.67
times for the lower temperature sintering to about 3 times
for the higher temperature sintering. By this discovery,
the inventors herein have determined an important
relationship between the growth of grain size and the
densification to permit relatively dense nanocrystalline
materials to be prepared from bulk or green nanocrystalline
20   material while limiting the grain growth to obtain a true
nanocrystalline material with suitable density and grain
size.

Nanocrystalline TiO_2 compacts were produced at Argonne.
Ti wire (99.99% purity) is evaporated in 500 Pa of He gas
(99.9999% purity) in a vacuum chamber that has been
evacuated to a typical pressure of 10^{-5} Pa prior to the
introduction of the He. Ultrafine gas-borne Ti powders are

formed due to collisions between the Ti vapor and the He and are collected on a liquid-nitrogen-filled cold finger. After completing the evaporation process, the vacuum chamber is again pumped to 10^{-5} Pa and the cold finger is warmed to room temperature. The Ti powder is then spontaneously oxidized to TiO_2 by the rapid introduction to the chamber of approximately 5kPa of O_2 gas (99.98% purity). After again evacuating the chamber, the powder is removed from the cold finger using a Teflon (registered trademark of DuPont) annular ring and is transported by gravity to a two-step in-situ compaction device. Finally, the powders are consolidated in vacuum at ambient temperature under high pressure (typically 1.4 GPa). The samples produced are in the form of disks having a diameter of 9mm and typical thicknesses of 0.1 to 0.5 mm.

The samples were sintered in the Los Alamos microwave processing facility. This 2.45 GHz microwave facility consists of a 6 kW microwave power supply, a .028m^3 resonant cavity equipped with a rotating specimen table and a two-color infrared pyrometer. Each sample was positioned between three low density ZrO_2 insulating blocks that were stacked and placed on the specimen platform in the cavity. The blocks were 6.35 cm diameter square, 3.8 cm thick. The center block contained a hole with a groove on the bottom in which the samples were mounted on edge. Temperature was monitored pyrometrically using a sapphire light pipe positioned approximately 3 mm from the sample. The green

compacts were processed under flowing argon. Each sample was heated rapidly from ambient to a maximum temperature of 800, 1000 or 1200°C and then the power was immediately cut off and the samples were allowed to cool. The time versus temperature curves are shown in Figure 1.

Green densities were estimated by weighing each sample and measuring the disk dimensions with a micrometer. The results are indicated in Table 1. This technique insured minimal contamination of the nanocrystalline TiO_2 samples prior to sintering, but typically gave lower density measurements than were obtained by Archimede's method. Archimede's method employed by weighing samples in air and in either deionized water or 1,1,1 trichloroethane, was used to determine accurate densities and open pore content of the samples following sintering, as well as to determine the density of one unsintered control sample.

Powder x-ray diffraction techniques using Mo-Kα radiation (_λ_ = 0.071 nm) were used to determine the crystalline phases present in the samples and to estimate the average grain sizes. The samples were mounted on a Lucite holder. X-ray collimation at the sample was about 1 cm x 1 cm. Data analysis was performed using a background correction program and a peak fitting algorithm. The full-width at half-maximum intensity (FWHM) of the fit was used with the Scherrer equation to obtain the grain size estimates. Samples were also examined using transmission electron microscopy before and after sintering. Grain size

histograms were obtained from diffraction-contrast dark-field images taken with JEOL 100CX operated at 100 kV. Samples were obtained by breaking small fragments from the disk edge with a sharp pair of tweezers and then dragging a C-coated Cu grid through this residue or by rubbing the grid over the surface of the sample. Each sample was also examined before and after sintering using He^+ and He^{++} Rutherford backscattering spectrometry (RBS) at both 2.2 and 8.8 Mev.

10   Table 1.   Grain size/density data for microwave-sintered nanocrystalline TiO_2.

Maximum Sintering Temperature	Density Initial (Direct)	(%Theoretical) Final (Archimedes)	Grain Size After Sintering (nm) Dark-field TEM	X-ray
Pristine*	54.9	70.4	14	8
800	61.7	68.7	16	9
201000	53.8	87.3	28	19
1200	59.6	92.8	18	35

*Rutile theoretical density = 4.26 g/cm^3.

The changes in density and grain size of nanocrystalline TiO_2 compacts resulting from the microwave sintering treatments are summarized in Figure 2 and Table 1. The samples were observed to have very high green densities (~70% of theoretical). Microwave-sintering at maximum temperature of $\leq$ 800°C had little effect on either the density or grain size of the samples. It was observed that

nanocrystalline TiO_2 could be sintered to almost 90% of theoretical density in very short times while maintaining a grain size of less than 20 nm when microwaved to a maximum temperature of 1000°C. This is a significant improvement over the behavior of nanocrystalline TiO_2 samples that were sintered conventionally at lower temperatures for much longer times. A comparison of the present results with data obtained by prior art sintering is shown in Figure 3. Increasing the maximum microwave-sintering temperature to

10   1200°C increased the density to above 93%, but at a cost of increasing the grain size to 35 nm. However, it should be noted that the heat-up rate for the 1200°C sample was somewhat lower than that for the 1000°C sample. The density results indicate that most of the porosity in the samples is open until the total density approaches 90% of theoretical. TEM observations revealed no evidence of abnormal grain growth.

It was found that TEM and x-ray techniques yielded somewhat different values for the measured average grain

20   sizes, with the TEM values being larger than the x-ray values for the pristine, 800° and 1000° samples, but smaller for the 1200° sample. There are several possible reasons for this behavior. The x-rays penetrate more than 50 microns into the sample while the TEM samples used in this study were obtained only from the outer surfaces of the sample. Thus, it is possible that this indicates that the sintering behavior at the sample surfaces differs from that

in the bulk. This is not surprising because the green

compacts always have a rather low density outer rim and most

of the material used for TEM samples comes from this area.

For this reason we believe the x-ray results are more

meaningful, particularly for the 1000 and 1200°C samples.

However, the x-ray results are also subject to potential

artifacts, primarily due to either the background

contributions from the sample holder or the contribution of

strain in the samples to the broadening of the diffracted

10   peaks. If the residual strain in the sample is significant,

the Scherrer formula will underestimate the true average

grain size. The presence of strain in a sample is indicated

by a systematic change in apparent grain size as 2-theta

increases. Such behavior was seen in the x-ray data

obtained from the pristine and 800°C samples. The 1000° and

1200°C -sintered samples were initially even more highly

strained than the other two samples (they were visibly

bowed), but the strain was released by breaking the samples

into fragments. These fragments showed no sign of residual

20   strain and thus we believe the grain size values obtained

from them were accurate.

X-ray diffraction revealed the samples to consist of

primarily the rutile phase of TiO_2, but small amounts (order

of 5%) of anatase TiO_2 were also seen in the pristine and

800°C-sintered samples. No sign of anatase was seen in

either sample heated to higher temperatures. Samples

underwent both shape and color changes as a result of the

sintering process. The samples were originally black, but
took on an increasingly yellowish appearance following
sintering with the higher temperature-sintered samples
showing more yellow than the 800°C sample, which had only a
yellowish-appearing rim. The samples also showed
appreciable warpage and cracking at higher temperatures.
RBS data showed no change in oxygen content as a result of
sintering in argon. Thus the color changes in the samples
are presumably correlated with changes in grain size.

10   Analyzing the data set forth herein, it will be seen
that a relationship exists between the sintering temperature
expressed as a percent of the melting point in degrees K and
the increase in the grain size from the bulk sintered
material.

      For instance, the melting point of rutile TiO_2 is
2143°K and 1000°C (1273°K) is about 59% of the melting
point. Rutile TiO_2 produced in bulk has an average grain
size of about 12 nanometers while the 90% theoretical
density material produced by microwaving the material to a
20   temperature of 1000°C or 1273°K produces an average grain
size of about 20 nanometers. The increase in grain size is
about 67%. Exposing the rutile TiO_2 to microwave energy
until temperatures of about 59% of the melting point of the
material (expressed in degrees Kelvin) are reached results
in grain growth of about 67% and increase in density to
about 90% of theoretical. Nanocrystalline magnesium oxide
in bulk (green) form has an average grain size of about 5

nanometers and the melting point of magnesium oxide is 3,073°K (2800°C). Microwaving nanocrystalline magnesium oxide to about 59% of its melting point or about 1540°C will produce grain sizes of about 8-1/3 nanometers. On the other hand, by exposing rutile TiO_2 to temperatures of 1200°C or about 70% of the melting point (2143°K) of the rutile TiO_2, the density is increased from about 90% to about 95% but the grain growth instead of being increased 67% is now a 200% increase so that 12 nanometer bulk (or green) material now has an average grain size of about 35 nanometers. For magnesium oxide, an exposure to microwave energy to about 70% of its melting point or about 1878°C (2151°K) results in a 95% dense material having an average grain size of about 15 nanometers.

Since the grain size grows exponentially as the sintering temperature increases, it will be seen that very rapid grain growth occurs at temperatures above about 70% of the melting point of the nanocrystalline material (expressed in degrees Kelvin).

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

Abstract Of The Invention

A method of sintering nanocrystalline material is disclosed wherein the nanocrystalline material is microwaved to heat the material to a temperature less than about 70% of the melting point of the nanocrystalline material expressed in degrees K. This method produces sintered nanocrystalline material having a density greater than about 95% of theoretical and an average grain size not more than about 3 times the average grain size of the nanocrystalline material before sintering. Rutile TiO_2 as well as various other ceramics have been prepared. Grain growth of as little as 1.67 times has resulted with densities of about 90% of theoretical.
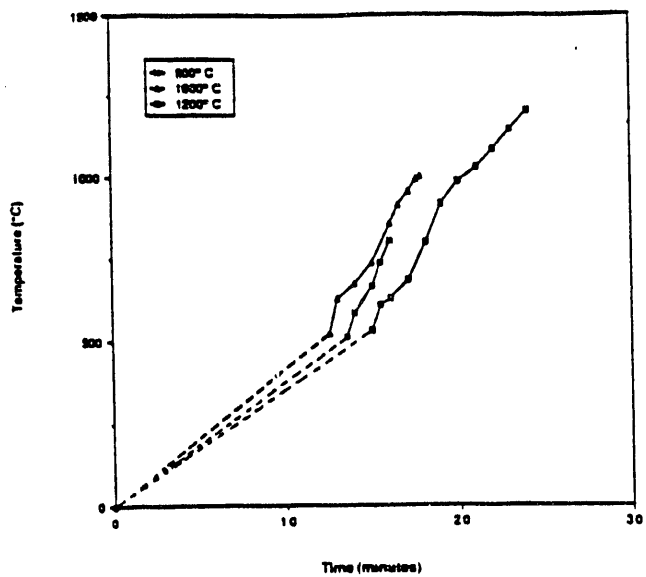
Fig. 1
Time-temperature curves
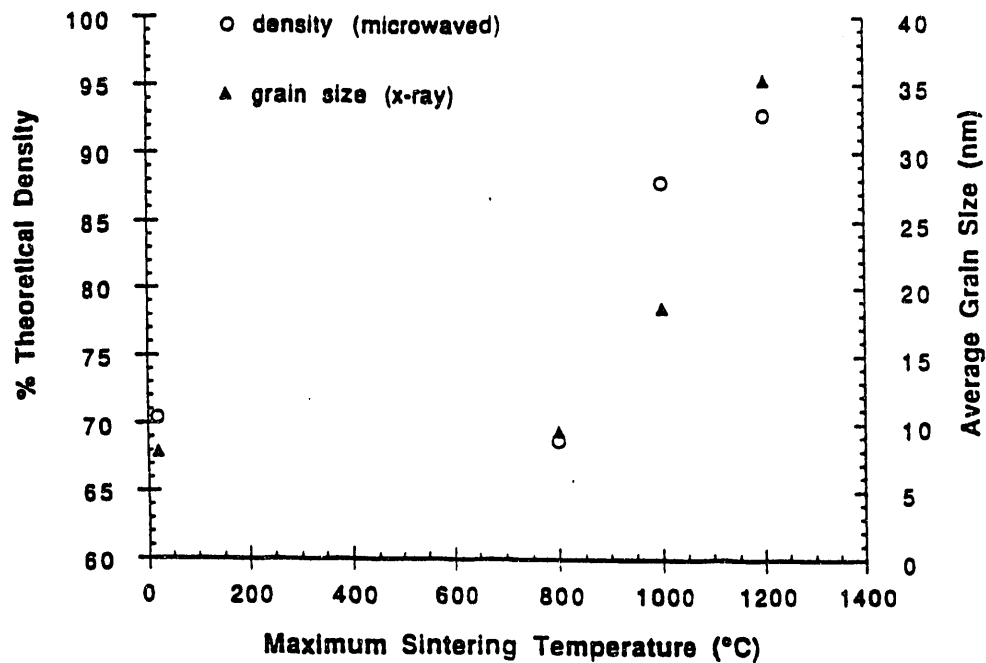for each of the microwaved
samples.

Fig. 2
Grain size and density versus maximum sintering temperature for the microwave sintered samples.
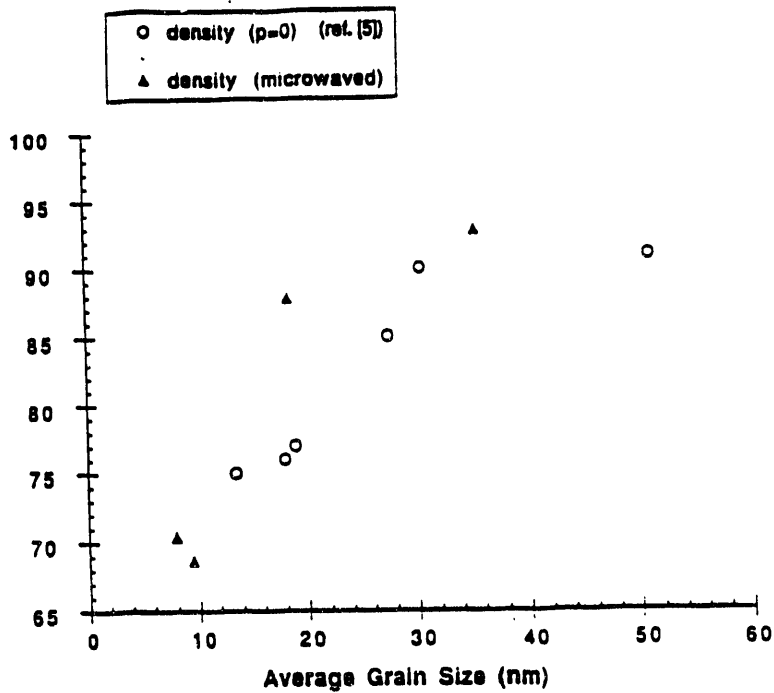
Fig. 3
Grain size versus density
plot showing a comparison
of microwave sintering with
           conventional
longer time, lower temperature
sintering results.

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