Microwave Processing

CONTINUOUS MICROWAVE-DRIVEN POLYOL PROCESS FOR SYNTHESIZING YTTERBIUM-DOPED YTTRIA POWDER

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ABSTRACT

The continuous microwave polyol process is a promising novel approach to the synthesis of metallic and ceramic nanopowders. Current efforts are directed toward synthesizing ytterbia-doped yttria (Yb_2O_3:Y_2O_3) for use as a polycrystalline laser host material. The process involves pumping a mixture of yttrium nitrate and ytterbium nitrate dissolved in hydrated diethylene glycol through a pressurized quartz tube contained in an S-Band waveguide driven by a 2.45 GHz microwave source at powers up to 6 kW. As the solution moves along the waveguide, it absorbs the co-propagating microwave energy and is heated rapidly to a temperature above 200°C causing a reaction to occur. Condensation reactions then form particles with ytterbium-doped yttria crystal structure. The rapid heating and cooling serve to limit the growth of the crystals so that they are on submicron and fairly uniform in size. The production of doped yttria was confirmed by x-ray diffraction.

INTRODUCTION

In the polyol process, an organic solvent such as glycol or alcohol is used to reduce a dissolved metal salt to the metal [1,2]. This is commonly done in a boiling, reflux system where the glycol solution of the metal salt is heated to boiling, and the evaporating solvent is condensed and fed back into the solution. At the elevated boiling temperature, the glycol solvent acts as a reducing agent, converting the dissolved metal salt first to a metal oxide and then to the metal. The process results first in the formation of metal atoms suspended in the glycol solvent. These then aggregate, first into clusters and then into larger metallic particles. The process is capable of producing metallic particles in the nanometer size range (1-100 nm), and the particles produced are protected from oxidation or nitridation by the organic solvent and can also be further protected by organic coatings generated during the process from additives.

This process has been used for about a decade in production of nanophase powders of metals and mixtures of such metals and films or coatings of these [3], and a wide range of metals can be produced in this manner. The process can also be used to produce metal oxides, sulfides and selenides [4,5]. The limiting factor is the chemical energy available from the solvent vs. the enthalpy of formation of the metal oxides. This makes it very difficult to obtain nanophase metals such as lithium, aluminum, yttrium, magnesium, zirconium, e.g., Groups I-IV, without resorting to much higher processing temperatures, although nanophase *oxides* of many of these metals can be produced [6]. However, most of the balance of the metals in the periodic table can be produced by this process, e.g., Fe, Co, Ni, Cu, Ru, Rh, Pt, Au, etc., as well as intimate mixtures of these--Fe/Co, Co/Pt, Fe/Pt, Ni/Ag, Cu/Ni, Co/Ni, Co/Ni/Cu, etc.

The conventional polyol process, where the processing is done with a high boiling point solvent such as ethylene glycol, heated in a reflux system by a heating mantle, is adequate for production of small quantities of experimental powders, e.g., 1-10 g of product from a 1 liter batch that may take 0.5-2 hours to process. However, the process is intrinsically limited in scalability. In the heating mantle/flask system, scaling to larger volumes results in much greater product variability from varying thermal histories in the larger volume with different convection

cell structure, and also typically results in larger particle sizes from longer processing times. The typical approach for increasing production rates is to set up a large number of reactors running simultaneously. This approach raises issues of batch-to-batch and reactor-to-reactor product variability, and may never be capable of producing larger quantities for production uses at reasonable costs.

One process variation that has been adopted to overcome the limitation on process temperature resulting from boiling of the solvent is to drive the process in sealed containers heated in a microwave cavity [5-10]. This has been done using adaptations of systems intended for microwave digestion. This permits raising the process temperature to as high as 240°C vs. a boiling point for ethylene glycol of ca. 185°C, and avoids the complications associated with solvent boiling. While this process has some advantages over the conventional flask/heating mantle systems, it also has extreme limitations in terms of process size. The typical reactors, Teflon-lined PEI, that, in theory, are limited to temperatures of 170°C, are only 100 ml in volume. This permits production of only about 0.01 g of product per reaction vessel, typically processed in about 15 min. Again, this may be useful for preliminary research purposes, but is clearly not scalable. Going to larger reactors in a more powerful microwave system would result in unacceptably high stresses in the vessels (the stresses scale with reactor diameter), that are already being operated above their rated continuous operating temperature.

We have been investigating the use of microwave and millimeter-wave systems in various types of materials processing for about a decade [11-17]. As part of this program we have been exploring the use of microwave and millimeter-wave heating of polyol solutions for the production of nanophase metals and oxides.

EXPERIMENTAL

Initially, this process was demonstrated with millimeter-wave beam heating (83 GHz) of batch polyol systems [14]. This demonstrated that greatly reduced process times could be achieved with the millimeter-wave beam heating, which is capable of rapidly heating polyol solutions in bulk, but still left the problems with the economics of the batch process. Subsequently, continuous polyol processing with millimeter-wave beam heating was demonstrated with very interesting results. In this case, shown in Figure 1 an ethylene glycol/copper acetate solution was heated by the millimeter-wave beam to approx. 200°C in a few seconds as it passed through a silica reaction tube, approx. 10 mm in ID, producing nanophase copper metal particles from the copper acetate. This is an extreme case of microwave polyol processing, as the beam configuration permits very high deposited power densities in the solution, perhaps as high as 100-500 W/cm^3 in the liquid, but it's very interesting here that this process can be driven to completion in a few seconds in this continuous system, rather than the hours required in the conventional process.

Use of the millimeter-wave system for large scale production of nanophase metals was considered, but several practical considerations argued otherwise. The millimeter-wave system is very costly, high operating costs, and the continuous system involved extensive plumbing and plumbing connections within the millimeter-wave processing chamber, making operations and maintenance rather difficult and system reliability questionable. A continuous processing system is only economical when it can be operated continuously for long periods at low cost. These considerations led to the decision to use a dedicated, lower frequency, S-band source (2.45 GHz)

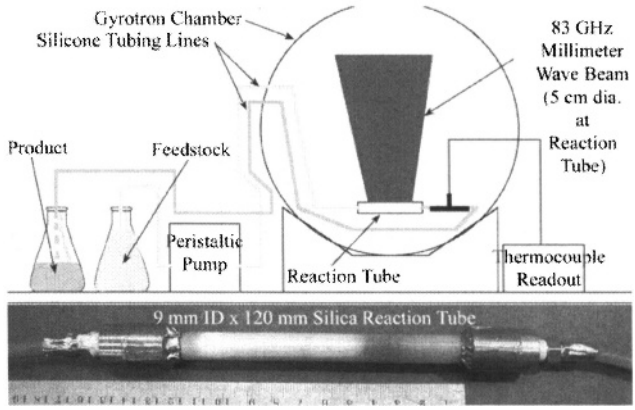

Figure 1. Schematic of millimeter-wave driven continuous polyol process using 83 GHz gyrotron source operating at 2-3 kW and producing nanophase copper with less than 10 s reaction time.

for a continuous microwave polyol system much more likely to be successful and economically feasible in large scale production of nanophase metals. One pleasing but fortuitous result with this change was much better coupling to the polyol solution. It happens that the peak in absorption in ethylene glycol is very close to 2.45 GHz; thus we have very efficient coupling at this frequency into small volumes of solution. The small volume consideration has significant implications for operation under pressure.

We initially experimented with an S-band analogue of the millimeter-wave system, using a resonant cavity made from a shorted waveguide section, tuned to place the maximum in the field at the location of a silica reaction tube passing transversely through the waveguide section. This was found to be impractical because of the field distribution within the cavity that resulted in a heated region only 1-2 cm in length, with inadequate time for the process to occur. We subsequently went to a traveling wave applicator that has been very successful for this process and provides a much better geometry for a well-controlled continuous polyol process [18]. This configuration is shown schematically in Figure 2.

In this system, the direction of propagation of the microwaves down the waveguide and the direction of flow of the polyol solution through the inner quartz tube can be in the same or opposite sense. These produce different temperature distributions in the polyol solution. Temperature distributions, based on modeling results, can also be controlled by variations in input microwave power vs. polyol flow rate. Presently, we are operating with the propagation and flow directions the same and with process parameters that result in a fairly uniform temperature distribution. The other choice, with the directions opposite, produces a more gradual temperature rise in the solution with a shorter length of fairly uniform temperature. For the case we are using, the liquid traveling down the tube is heated by absorption of the microwaves traveling down the waveguide, with the power deposited proportional to the electric

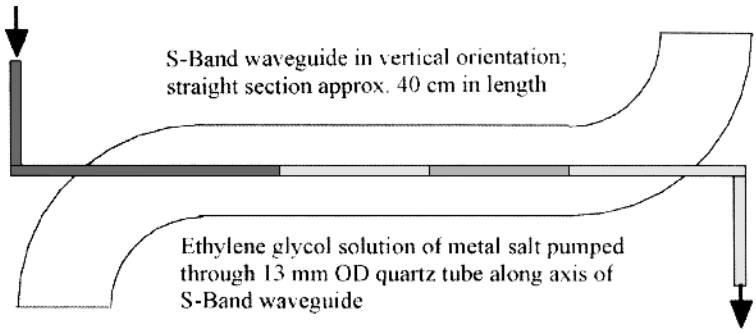

Figure 2. Schematic of microwave polyol process with solution pumped through silica tube placed along centerline of S-Band waveguide–the microwaves that propagate down the waveguide heat the solution flowing along the tube.

field squared and the dielectric loss in the liquid. The absorption in the liquid causes attenuation of the microwaves; in our present system and with our current operating parameters, all of the microwave power is absorbed in the polyol solution in a distance of 20-40 cm, as the solution is heated from its initial temperature to a maximum of 180-240°C (depending on system pressure) as shown in Figure 3. Because of the relatively simple geometry and well-defined boundary

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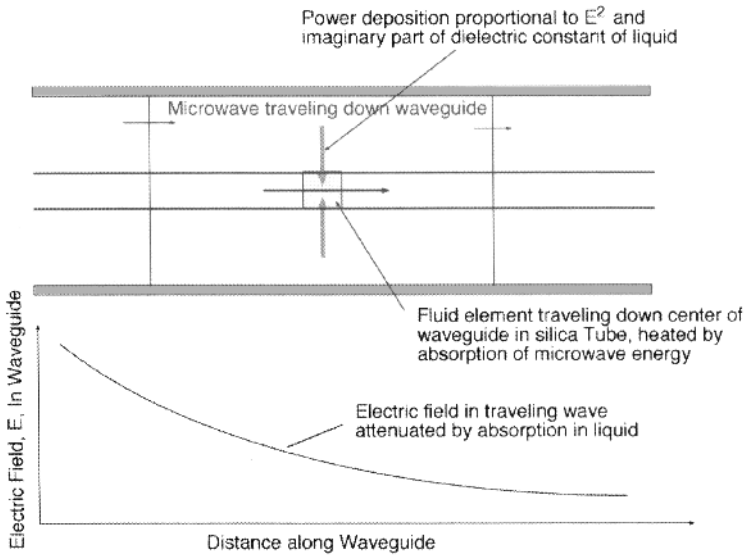

Figure 3. Schematic of basis for model for waveguide microwave heating of flowing polyol solution

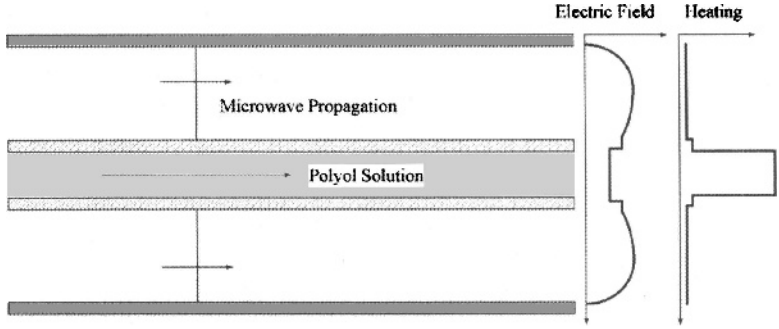

Figure 4. Schematic of electric field distribution in waveguide containing silica tube with flowing polyol solution; field in polyol solution is reduced because of high permittivity (dielectric constant), but energy absorption is highly localized in polyol solution because of very high dielectric loss.

convection in a closed system) and from the outside of the waveguide (free convection), though these are not significant, corrections with present conditions. Other thermal losses (radiation, conduction) are negligible. With present parameters, the outside of the waveguide, cooled by

free convection, remains below 60°C, with the polyol solution at 240°C. The result of these calculations, as confirmed by experiments with thermocouple probes at various locations in the polyol solution is a rapid increase, over about 10 cm, in temperature of the polyol solution to a plateau value as shown in Figure 5. This plateau value is maintained, for appropriate choices of microwave power

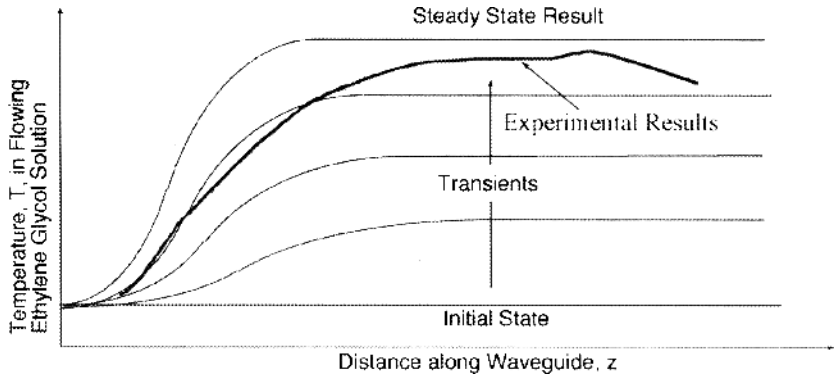

Figure 5. Schematic of temperature distribution in continuous microwave polyol system with polyol flow and microwave propagation directions coincident with experimental results shown for comparison.

and solution flow rate, over a substantial distance--30-60 cm. With this present arrangement, the solution being processed can be maintained at a desired process temperature over this distance which corresponds to a residence time, in the reaction tube of 30-60 s. With this system at ambient pressure, temperatures slightly in excess of boiling can be reached, approx. 180-200°C, for ethylene glycol solutions. We currently are operating the system at an overpressure of 0.2-0.3 MPa, using pressure regulators on the outlet side and positive displacement pumps to move the solution, and thus can operate at about 240°C, without boiling occurring. The use of this overpressure is greatly facilitated by the relatively small diameter of our silica processing tube that should be capable of operating at pressures as high as 70 MPa. An overall picture of the actual system is shown in Figure 6. This is a somewhat earlier version of the system but shows most of the current features. The S-Band source is to the left in a self-contained unit, ~1.5 m in height and 1 m in width, and requires 440V, 30A three-phase electrical power as well as cooling water. The power is taken out of the unit on the top through conventional aluminum and brass waveguide. The working portion of the waveguide, containing the silica reaction tube for the polyol, is placed vertically here. Any power not absorbed in the polyol process is collected in a water load at the upper right of the waveguide. Input power to the system is monitored as well as power reflected back into the source. If needed, power into the water load can be monitored as well either by RF power meters or by measurement of cooling water temperature load. During normal operations, temperature of the polyol solution is monitored at the outlet (at the top). A well either by RF power meters or by measurement of cooling water temperature load. During

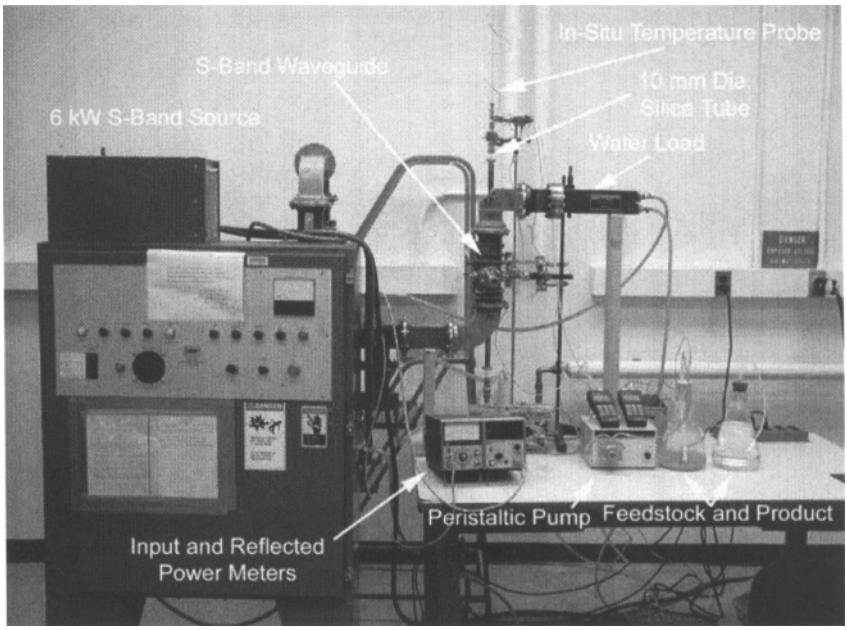

Figure 6. Overall view of continuous microwave polyol system based on 6 kW maximum output S-Band, 2.45 GHz source.

normal operations, temperature of the polyol solution is monitored at the outlet (at the top). A fine wire thermocouple probe can be used, if necessary to check the temperature at various points along the length of the reaction tube, but is normally not needed with stable continuous operation. Viewports are also available which can be used to observe the process visually at roughly the midpoint of the reaction tube. The system is currently being operated under overpressure; this is achieved via a positive displacement pump driving the polyol solution, currently capable of achieving about 0.7 MPa pressure. The pressure is controlled via a pressure regulator on the outlet. The product solution is rapidly cooled via a stainless steel heat exchanger in an ice water bath and collected for use or analysis. Nearly all of the parts of the present system through which the reactants and products pass are either stainless steel or silica, with thick wall silicone rubber tubing used in some areas. These components will tolerate the reactants used, the temperatures involved (currently up to 240°C), and the overpressures used to suppress boiling. The entire system will tolerate cleaning operations such as flushing with nitric acid to remove metallic residues, followed by distilled water, alcohol and ethylene glycol flushes. This capability is critical if the system is to be used for more than one type of material and purity of products is critical.

In the present work, the chemicals used were diethylene glycol (Alfa Aesar), yttrium nitrate (99.999%, Metall), ytterbium nitrate (99.99%, Metall), urea (Fisher Chemical), and

distilled water. Diethylene glycol was used instead of ethylene glycol to minimize the onset of boiling during processing as it has a higher boiling point. Three thermocouples were used to monitor the process at various points—one at the intake flask, another after the waveguide to measure internal temperature, and another at the collection flask to determine how much the solution has cooled after going through the cooling coil. An S-Band 2.45-GHz Cober high power microwave generator provided the power. The pump system was made up of a peristaltic pump, quartz tubing through an s-band waveguide, a stainless-steel pressure-regulation system, and rubber tubing that led to a stainless-steel cooling coil in a water bath as shown in Figure 6. A precursor solution was created containing diethylene glycol, yttrium nitrate, and ytterbium nitrate. Dissolving agents and catalysts, urea and water, were also added to the solution. Each run contained 1200-mL of diethylene glycol, 30-mL of water, and 24-g of urea. The amount of yttrium nitrate and ytterbium nitrate was determined by weight according to the dopant concentrations of 0%, 5%, and 10%. When mixing the precursor solution, a magnetic stirrer and a hot plate were used to warm the mixture to 70°C, until homogeneous. Before the precursor solution is pumped through the system, the reaction pathway is primed with pure diethylene glycol to eliminate air from the system. Next microwave power is increased slowly until a temperature of ~ 212°C is achieved at the waveguide output at a pressure of 20-psi. This temperature and pressure is maintained as the solution is pumped at 0.37 mL/s through the system and collected in a flask that was maintained at room temperature.

The solution is then cleaned in an alcohol rinsing procedure, which requires a centrifuge. The solution is first put in centrifuge tubes and centrifuged for 30-min at 10,000-rpm. The diethylene glycol is then decanted. The tubes are then filled with the alcohol reagent and spun for 15-min at 10,000-rpm two more times. The result was a highly compacted white paste. The paste was then placed on a Petri-dish and warmed to 70°C in open air to evaporate off the alcohol reagent. The powder was calcined in a furnace for 150-min at about 700°C. The resulting powder is analyzed using x-ray diffraction and scanning electron microscopy.

X-ray diffraction scans on Y_2O_3 and Yb_2O_3 powder samples were obtained using Cu Kα radiation from a rotating anode x-ray source and a high resolution powder diffractometer. Figures 7a shows the scan taken for Y_2O_3 samples after microwave processing. The vertical lines correspond to the expected diffraction pattern for Y_2O_3 from JCPDS card (Pdf # 00-043-1036) [19]. It is clear from these figures that a pure Y_2O_3 phase was obtained although in Fig. 7a we also see some extra peaks that are not identifiable. Figures 8a and 9a correspond to a mixture of Y_2O_3 with 5 and 10 % Yb_2O_3 respectively. Superimposed on these scans are the red vertical lines corresponding to pure Y_2O_3 phase and blue vertical lines (Pdf # 00-043-1037) [19] corresponding to Yb_2O_3. As can be seen there is a shift between in the position of the peaks with their centroids located in between these two vertical lines. This indicates a change in lattice parameters with increasing Yb_2O_3 composition and also the ytterbium is occupying the yttrium site substitutionally. This is expected if a solid solution is formed between Y_2O_3 and Yb_2O_3 since both are isostructural having a space group Ia3(206) [20].

SEM micrographs. Figures 7b, 8b and 9b, show particle size ranging from 400 to 700 nm. We did not attempt to control the particle size by regulating flow rate or temperature.

DISCUSSION

The steps of reaction for the formation of yttrium oxide can be assessed through the color changes during processing. The solution is initially clear, precipitation occurs while heating and becomes translucent, and then slowly changes to milky-tan. These reaction steps indicate that

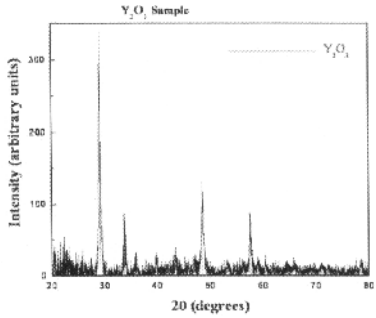

Figure 7a. X-ray diffraction scans on Y_2O_3 sample obtained by polyol processing

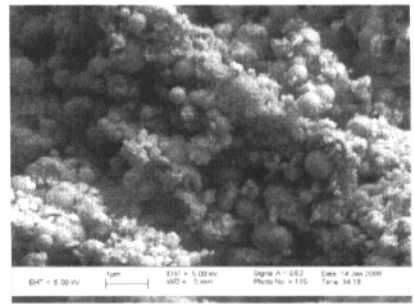

Figure 7b. SEM micrograph of Y_2O_3

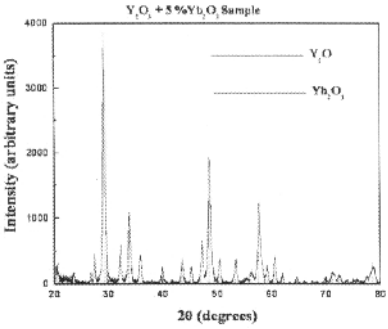

Figure 8a. X-ray diffraction scans on Y_2O_3 + 5 wt%Yb_2O_3 sample obtained by polyol processing

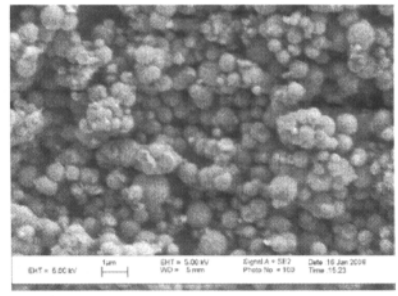

Figure 8b. SEM micrograph of Y_2O_3 + 5 w(%Yb_2O_3

the precursor first reacts to form an insoluble intermediate, which then slowly becomes yttria by means of a continuous reaction. A likely mechanism for this reaction is given below:

$$(1) \qquad Y(NO_3)_3 + OH^- \rightarrow Y(NO_3)_x(OH)_{3-x} \rightarrow Y(OH)_3$$

$$(2) \qquad Y(OH)_3 \rightarrow Y(OH)_x O_{3-x} \rightarrow Y_2O_3$$

A similar reaction should apply for the formation of ytterbium oxide from ytterbium nitrate Doping essentially involves introducing an active ion into the crystal lattice. In order to create a good material, there needs to be a homogeneous mixture of the ytterbium oxide within the

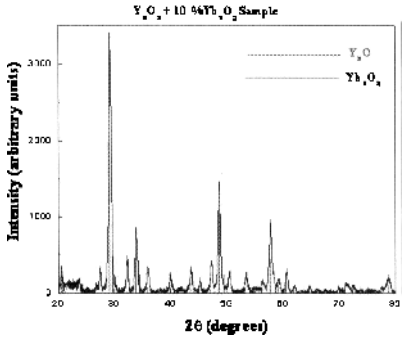

Figure 9a. X-ray diffraction scans on Y_2O_3 + 10 wt%Yb_2O_3 sample obtained by polyol processing.

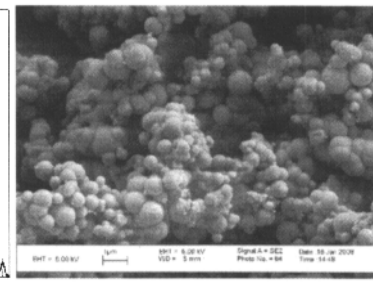

Figure 9b. SEM micrograph of Y_2O_3 + 10 wt%Yb_2O_3.

yttrium oxide crystal structure. By using diethylene glycol in the process, the ytterbium nitrate and yttrium nitrate can be suspended in solution to create a homogeneous solution. The suspension results in a dispersion that helps to create a well dispersed ytterbium-yttrium oxide structure. The resulting powder should have the proper proportions of ytterbium and be evenly distributed since the solution itself was evenly distributed. X-ray diffraction results give the indication that ytterbium was introduced into the yttrium crystal lattice as substitutional element.

To date, we have demonstrated that the continuous microwave polyol system can be used in production of sizeable quantities of nanophase ytterbium doped yttrium oxide. The process is energy efficient and can produce material with the purity level determined by the precursor materials. The particle size can be controlled which may help in further processing by optimizing temperature, pump speed, and pressure to fully take advantage of the microwave-assisted polyol process. Note that one significant advantage of operation under overpressure is the ability to use lower boiling point solvents or glycols that typically have higher solubility for the metal salts used as precursors. This could be useful in increasing production rates for materials whose precursors have very limited solubility in high temperature diols such as ethylene glycol. Another approach that may be possible to increase production rates, but has not been explored by the authors, is to employ suspensions of fine particles of precursors in a diol. This would eliminate the restrictions on concentrations imposed by solubilities, but might lead to larger metal particle size in the product because of the very different reaction path.

The economics of this process should be far superior to any of the batch polyol processes with much larger production quantities. We would expect that the process here could be readily scaled to higher production quantities. One obvious approach is to move to a higher power S-Band microwave source. The higher power, coupled with either a larger reaction tube and/or higher flow rates, would permit production rates several times higher than possible with our prototype system. A limitation with this approach is the high loss in solvents such as ethylene glycol, which limit the penetration depth of microwave energy. For sufficiently large reaction tubes, heating would no longer be relatively uniform across the diameter of the tube and greater process variability would occur. Another, also relatively practical scaling approach, is to move to a lower frequency system, such as L-band (915 MHz) for which low cost, commercial sources and hardware are also available. In this case, with a frequency about 1/3 that of S-band, the

waveguide are approx. 3 times larger, the absorption is somewhat less than at S Band, and reaction tubes 3-4 times larger than our 10 mm ID could easily be accommodated. An L-Band system, with a 40 mm ID reaction tube, and about 100 kW output, could process hundreds of liters of solution per hour and produce tens of kilograms of nanophase product per shift.

There are a number of cautions that need to be cited here. While the economics of the continuous microwave polyol process are quite good, with low capital cost, low operating and labor costs, and low raw materials cost, there are some other critical issues. One is the matter of recovering the nanophase metal or other powder product from the diol solvent and other reaction products. This is done on small scales now, but economical processes (settling, centrifuging, ultrafiltration, controlled agglomeration) need to be available for the separation process on much larger scales. There are also generic problems associated with handling nanophase powders, which tend to agglomerate readily and are highly reactive with atmosphere, but these are not peculiar to polyol-derived nanophase powders. Processing hundreds or thousands of liters of glycol solution per shift also require economical techniques for recycling large quantities of usable solvents and reactants and disposing of waste products, that may or may not be hazardous. Assuming that these problems noted here could be overcome, the continuous microwave polyol process could be a viable technique for economical large-scale production of a wide range of nanophase materials–metals, metal alloys and mixtures, metal oxides and other materials such as selenides and sulfides.

CONCLUSIONS

1. The continuous microwave polyol system can be used in production of sizeable quantities of nanophase ytterbium doped yttrium oxide.
2. The economics of this process should be far superior to any of the batch polyol processes.
3. X ray diffraction results give the indication that ytterbium was introduced into the yttrium crystal lattice as substitutional element.
4. A likely mechanism for the formation of ytterbia/yttria from ytterbia/yttria nitrate is proposed.

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FOOTNOTES

* Summer student

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REFERENCES

[1]D. Lewis III, M. A. Imam, R. W. Bruce, L. Kurihara, A. W. Fliflet and S. H. Gold, Production of Nanophase Metals via the Continuous Microwave Polyol Process, TMS Proceedings on Powder Materials, pp.157-168 (2003)

[2]D. Larcher and R. Patrice, Preparation of Metallic Powders and Alloys in Polyol Media: A Thermodynamic Approach, J. Solid State Chem. **154,** 405-411 (2000).

[3]G. M. Chow, J. Zhang, Y. Y. Li, J. Ding and W. C. Goh, Electroless polyol synthesis and properties of nanostructured Ni_xCo_{100-x} films, Mater. Sci. and Eng. **A304-A306**, 194-199 (2001).

[4]D. Chen, G.Z. Shen, K. B. Tang, X. Jiang, L. Y. Huang, Y. Jin and Y. T. Qian, Polyol mediated synthesis of Nanocrystalline M3Sb83 (M=Ag, Cu), Mater. Res. Bull. **38** (3) 509-513 (2003)

[5]H. Grisaru, O. Palchik, A. Gedanken, V. Palchik, M. A. Slifkin and A. M. Weiss, Preparation of the Cd(1-x)Zn(x)Se alloys in the nanophase form using microwave irradiation, J. Mater. Chem. **12** (2) 339-344 (2002)
[6]T. Yamamoto, Y. Wada, H. B. Yin, T. Sakata, H. Mori, S. Yanagida, Microwave-driven polyol method for preparation of TiO2 nanocrystallites, Chemistry Letters **10,** 964-965, (2002).
[7]M. Tsuji, M. Hashimoto and T. Tsuji, Fast Preparation of Nano-sized Nickel Particle Under Microwave Irrad. without Using Catalyst for Nucleation, Chemistry Letters. 1232-1233 (2002).
[8]W. Tu and H. Liu, Rapid synthesis of nanoscale colloidal metal clusters by microwave irradiation, J. Mater. Chem. **10**, 2207-2211 (2000).
[9]S. Komarneni, L. Dongsheng, B. Newalkar, H. Katsuki and A. S. Bhalla, Microwave-Polyol Process for Pt and Ag Nanoparticles, Langmuir 2002, **18** 5959-5962 (2002).
[10]D. Li and S. Komarneni, Microwave-Assisted Polyol Process for Synthesis of Ni Nanoparticles, Journal of the American Ceramic Society **89**, 1510 – 1517(2006)
[11]R. W. Bruce, A. W. Fliflet, D. Lewis III, R. J. Rayne et al., Microwave Sintering of Pure and Doped Nanocrystalline Alumina Compacts, Mat. Res. Soc. Symp. Proc., **430**, 139-144 (1996).
[12]R. W. Bruce, A. W. Fliflet, R. P. Fischer, D. Lewis III et al., Millimeter Wave Processing of Alumina Compacts, Ceramic Transactions Vol. 80 Microwaves: Theory and Application in Materials Processing **IV**, 287-294 (1997).
[13]A.W. Fliflet, R. W. Bruce, R. P. Fischer, D. Lewis III, L. K. Kurihara, B. A. Bender, G.-M. Chow and R. J. Rayne, A Study of Millimeter-Wave Sintering of Fine-Grained Alumina Compacts, IEEE Trans. On Plasma Sci., Vol. 28 No. 3, 924-935 (2000).
[14]L. K. Kurihara, D. Lewis, A. M. Jung, A. W. Fliflet and R. W. Bruce, Millimeter-Wave Driven Polyol Processing of Nanocrystalline Metals, Proc. MRS. Vol. 634 (2001)
[15]S. H. Gold, D. Lewis, A. W. Fliflet, B. Hafizi and J. R. Peñano, Interference and Guiding Effects in the Heating of Ceramic Slabs and Joints with Millimeter-Wave Radiation, J. Mater Synth. and Proc., **9**, No. 5 287-297 (2002).
[16]D. Lewis, M. A. Imam, L. K. Kurihara, A. W. Fliflet, S. Gold, R. W. Bruce, Material Processing with a High Frequency Millimeter-Wave Source, Mater. and Manuf. Proc., **18,** No. 2 151-167 (2003).
[17]M. A. Imam, D. Lewis III, R. W. Bruce, A. W. Fliflet and L. K. Kurihara, Processing of Advanced Materials with a High Frequency, Millimeter-Wave Beam Source and Other Microwave Systems, Materials Science Forum, **426-432**, 4111-4116 (2003).
[18]S.H. Gold, R.W. Bruce, A.W. Fliflet, D. Lewis III, L.K. Kurihara, and M.A. Imam, System for Continuous Production of Nanophase Material using a Microwave-Driven Polyol Process. Rev. Sci. **78**, 023909, pp. 1-6 (2007)
[19]MacKenzie, K.J.D., Gainsford, G.J., Ryan, M.J. J. Eur. Ceram. Soc., v16 p553 (1996)
[20]Zachariasen, W.H. Skr. Nor. Videnskk.-Akad., Kl. 1: Mat.-Naturvidensk. Kl., v1928 p1 (1928)