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Processing of Advanced Materials with a High Frequency, Millimeter-Wave Beam Source and Other Microwave Systems

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Abstract. An 83 GHz gyrotron-based, millimeter-wave beam system is being used in material processing: in rapid sintering of oxides, ferrites, and metal-ceramic composites to retain very fine grain structure in the product for improved mechanical and electromagnetic properties; in joining of ceramic and ceramic composite materials (with unique advantages– localization of heating, permitting inexpensive fixturing and instrumentation and minimizing thermal damage to components; depositing energy specifically in a narrow joint region through a guided wave effect), and in coating densification and coating removal where the high frequency and short wavelength permit significant energy deposition in relatively thin coatings. In a related effort, we are using a low frequency microwave system for low cost continuous production of nanophase metals. This process should produce a range of nanophase metals, metal oxides and mixtures of these, in sizeable quantities and at low cost. The results of various experiments in these areas will be discussed, as will the potential of low and high frequency microwave processing of advanced materials.

Introduction

The authors have been investigating the use of microwave and millimeter-wave systems in material processing. Such systems can have unique advantages or capabilities vs. conventional material processing. We have investigated the use of 2.45 GHz and 35 GHz cavity systems in rapid thermal processing of ceramics [1-6]. We are currently using two particular systems: an S-Band, 2.45 GHz system for continuous production of nanophase oxides and metals, and an 83 GHz, millimeter-wave beam system for sintering, joining, coating and coating removal [7-13]. Presently, the S-Band system uses a waveguide or a resonant cavity, while the millimeter-wave system operates in a quasi-optical mode, with the millimeter-wave beam controlled by reflective optics.

Typically, microwave processing is promoted on the basis of thermal efficiency or rapid heating via in-depth energy deposition. We have been exploring the use of the millimeter-wave system in very rapid sintering of nanophase materials, particularly ferrites. Here, the in-depth heating permits very rapid processing (<10 minute cycles) intended to preserve very fine grain structure in the product. For small components, cycle times of less than 1 minute are possible. Theory suggests that the nature of the magnetic behavior of these ferrite materials is expected to change dramatically at grain sizes comparable to the magnetic domain. In the case of other materials, the fine grain size obtained leads to excellent mechanical properties and the possibility of superplastic net shape forming– a possible processing route for ceramics is rapid sintering of powder compacts to nanophase green parts, then consolidation to full density and simultaneous shaping via using superplastic forming.

We are also investigating the use of the millimeter-wave beam system in joining of ceramics, applying coatings to ceramics and metals, and removal of coatings from metals and composites. Here, the millimeter-wave beam system provides unique advantages. The heating effects can be confined to an area as small as a square centimeter, permitting very localized thermal processing.

In addition, through a guided wave effect, the millimeter-wave energy can be confined to a joint region as small as 50-100 microns for even more localized effects [10]. The short wavelength of the millimeter-wave energy, 3.6 mm in air, about 0.3-2 mm in most ceramics, permits deposition of significant amounts of energy in even relatively thin polymeric and ceramic coatings and films. The localization of heating here has several advantages. One is the ability to do rapid, localized high temperature processing, e.g., heat treating of joints in ceramics or densification of ceramic coatings, while minimizing damage to thermally sensitive components. The same advantage pertains in removing coatings from thermally sensitive substrates, e.g., aluminum, FRP, GRP. With the beam system, the localization of heating and lack of coupling of the millimeter-wave to metals permit the use of inexpensive instrumentation and base metal fixturing. This is a major advantage in joining of ceramics, where alignment and pressure on the joint must be provided during joining. In a conventional system, where everything is heated, such fixturing and instrumentation must survive the same thermal conditions as the joint. In joining of high temperature ceramics, this requires either superalloy or ceramic fixturing, at great cost and with long lead times.

We are using an S-Band (2.45 GHz) system in continuous production of nanophase metals and metal oxides. Here the interest has been in providing an economical, well-controlled continuous analog to the polyol process used extensively for production of nanophase metal powders [9,11]. In conventional and microwave batch polyol processing, the amounts of materials produced are very small (g/day) [14-16] and the resultant material costs are far beyond what most applications would support. We have developed a continuous microwave process that should be capable of producing much larger quantities (kg/day) at much lower cost and potentially of much higher quality.

Experimental Systems

S-Band Microwave Continuous Polyol Processing System. The system used for continuous microwave processing of polyol solutions is based on a commercial 2.45 GHz S-Band source designed for continuous operation at up to 6 kW (see Fig. 1). Initially, this system was used to drive a resonant cavity through which the polyol solution was pumped in a quartz reaction tube. Presently, this unit provides power to a single-pass waveguide reaction system, providing much better coupling of output power into the process (essentially 100%), and a much greater process reaction length. Here, the source, supplies power to the S-Band waveguide. In the vertical section of waveguide, a quartz tube, about 1 cm in I.D. passes through the center of the waveguide (at the location of greatest electric field). The polyol solution is pumped through this tube and can be heated to over 200°C over a length of 10-20 cm. The water load at the top right of the figure absorbs any excess power. At power levels of 2-2.5 kW, this system can process up to 50 liters of polyol solution per day. Polyol solution temperatures are monitored at the inlet to the system, the outlet from the system, and at various locations within the quartz reaction tube, using a custom, glass-sheathed thermocouple probe which travels down the centerline of the quartz reaction tube.

83 GHz Millimeter-Wave Beam Material Processing System. The other system currently in use (see Fig. 2 below) for material processing is based on an industrial 83 GHz gyrotron source, than can operate from 100W to 15 kW continuously, with output in a quasi-Gaussian beam, with wavelength in air of about 3.6 mm. The beam is steered and/or focused by reflective optics (typically Au-plated Cu mirrors). The output of the gyrotron is through a water-cooled CVD BN window, with a secondary BN window in the transition between the gyrotron and processing chamber for additional isolation of the gyrotron from the processing environment. The processing chamber is about 1 m^3 in volume, water-cooled, gas-tight, and can be pumped down to about 50 mTorr. The processing chamber includes an internal water load to absorb excess power. Various feedthroughs are included on the chamber ports for instrumentation (thermocouples and pyrometers), power (for specimen manipulators), liquids and gases (cooling, process fluids, process atmosphere) and vacuum connection. Access is through two doors, and the workpiece and associated fixturing is carried on a
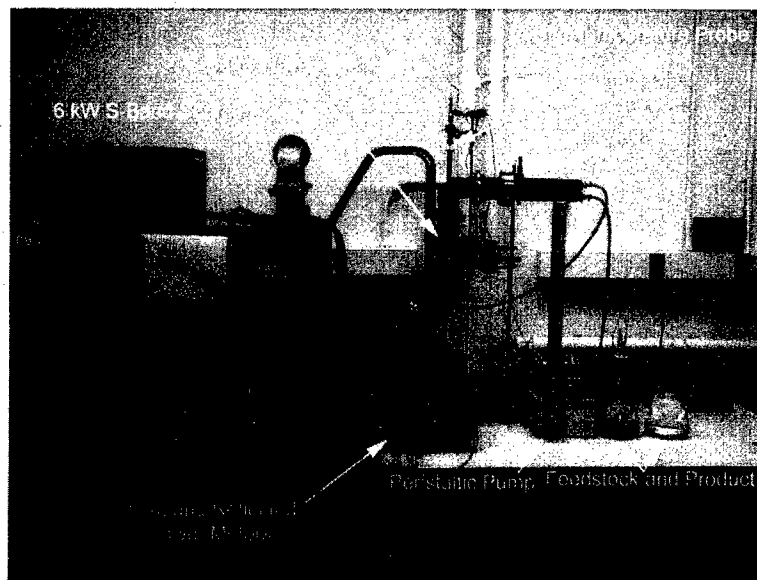
Fig. 1. S-Band, 2.45 GHz, waveguide system for continuous processing of polyol solutions to produce nanophase metal and metal oxide powders.

sliding tray that can be removed to the outside of the chamber through the large door at the left. The optics that focus and steer the beam are remotely controlled via the 4-axis manipulator on the top of the chamber. The system permits spot sizes of approx. 1-100 cm^2, with power densities ranging from about 10 W/cm^2 up to 10 kW/cm^2. The entire system is controlled by a high end PC running LabVIEW™ software, that collects a variety of process and operating system parameter data, is completely interlocked for safety, and can readily be controlled by a single operator.

Material Processing Experiments and Results

Continuous Production of Nanophase Metal Powders. The S-Band waveguide system shown above has been used in continuous production of nanophase Cu from a solution of copper acetate in ethylene glycol [11]. In this process, the hot solvent (glycol) is used to reduce the metal salt to first the metal oxide and then to the metal. The solvent also protects the metal powder produced from oxidation. The high boiling point of ethylene glycol, and the modest overpressure in our system, permit attainment of temperatures of ca. 210°C, and conversion of the copper acetate to copper metal in the approx. 30 s residence of the solution in the reaction tube. This compares to process times of ca. 1 hr in a batch polyol reflux process that handles 1-2 liters per batch. The waveguide system physics yield good process conditions with a substantial length of nearly uniform solution temperature in the reaction tube as shown both by calculations and by direct measurements of temperature distribution. The powders obtained in this process were approx. 10-100 nm in size. Similar results have also been obtained using a shorter reaction tube heated by the millimeter-wave beam, with higher power densities, and residence times of only 2-3 s [9], but S-Band offers significant advantages over the millimeter-wave–much lower system cost, and better coupling to ethylene glycol at 2.45 GHz vs. 83 GHz, and is preferred as much more practical. Earlier millimeter-wave batch processing experiments suggest that this technique will produce a wide range of metal, metal alloy and metal oxide powders [9]. In the millimeter-wave batch polyol process, we produced a great variety of nanophase metals and metal mixtures, e.g., Fe, Co, Ni, Cu, Ru, Rh, Pt, Au, Fe/Pt, Fe/Co,
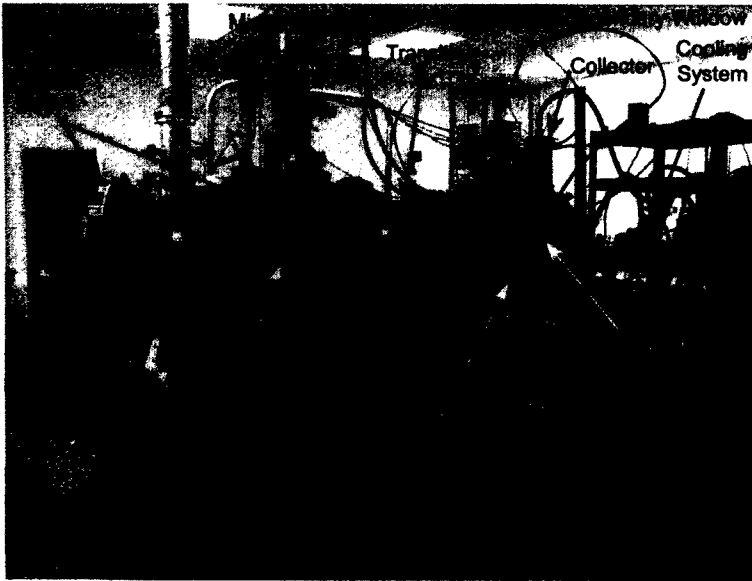
Fig. 2. 83 GHz millimeter-wave gyrotron-based material processing system used in rapid sintering experiments, coating deposition, coating removal and ceramic joining

Ni/Ag and Cu/Ni, and deposited nanophase Cu coatings on AlN substrates. It is expected that nearly all of the materials can be produced continuously in large quantities on the S-Band waveguide system, based on preliminary results and process kinetics.

Joining of High Temperature Ceramics. We have obtained strong, refractory joints in high temperature oxide ceramics, e.g., alumina, mullite, zirconia, with the millimeter-wave beam, We are using reactive oxide glass 'brazes' to join the ceramics, with heat treatment schedules (as in glass-ceramic processing) designed to react and interdiffuse the braze material with the adjacent ceramic, and recrystallize the products, producing a joint region with high ambient and elevated temperature strength, and which should have other properties (e.g., dielectric, thermal) comparable to those of the ceramics joined; see Fig. 3 below [13]. Using the beam system in joining has unique advantages over conventional methods: use of low cost metal tooling for component alignment and application of pressure to joints, and heating the immediate joint region and not the surrounding material or tooling, thus avoiding overheating of thermally sensitive components and tooling. We typically use steel tooling, and the tooling temperature never exceeds 50°C, with the joint region as high as 1900°C. Heating localization also permits simple instrumentation in the processing system, with conventional, unsheathed thermocouples, IR thermometers and two-color pyrometers used for temperature measurement. We provide for specimen translation and rotation with electrically driven stages operated through simple shielded cables. An example of the simple tooling possible is shown in Fig. 3d below which shows two machinist vises used to apply pressure during millimeter-wave joining of two alumina rods. In this case, a combined butt-lap joint was produced with a butt joint in alumina rods reinforced by a split alumina tube, and pressure was applied both along the length of the rods and in the transverse direction. Also visible is a metal foil radiation shield used both to confine the millimeter-wave radiation and minimize specimen radiative losses. BN spacers provide thermal and chemical isolation of the specimens being joined. We use BN for higher temperature fixturing because of its refractoriness, inertness, thermal properties and machinability. Its primary limitation is its tendency to oxidize under high temperature oxidizing conditions.

Heating Narrow Joints Using Guided Wave Effects. A unique feature of the millimeter-wave beam system we use is in the potential for localized heating of joints much smaller than the
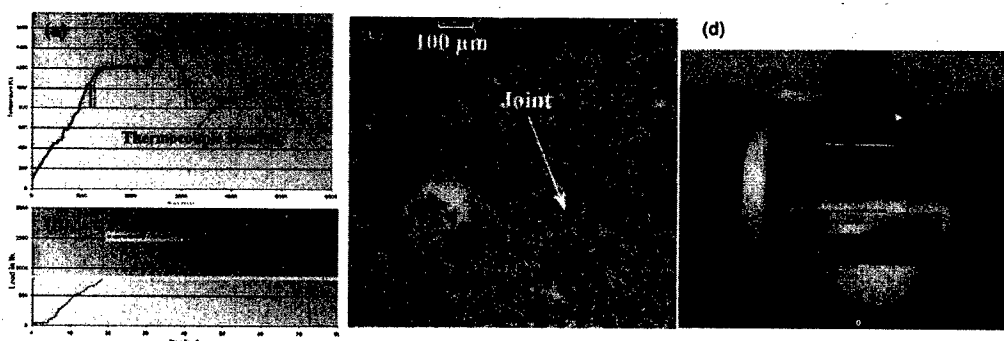
Fig. 3. (a) Temperature-time profile for producing high strength, refractory joint in high purity alumina with (b) shear strength of 120 MPa comparable to the alumina; (c) crystalline joint region indistinguishable from parent alumina material; (d) small and large machinist vises used to apply pressure in two orthogonal directions to butt-lap joint.

radiation wavelength [10], when the joint region is of higher dielectric constant than the adjacent material and relatively lossy. This can typically be achieved by metal powder-loaded ceramic brazes in the joint. Both calculations and experiments show that this technique will preferentially heat joints <100 µm in width and up to 1 cm in depth, and can be particularly useful when the material being joined is thermally sensitive, or it is desirable to minimize the size of the 'heat-affected zone'. In one experiment to join pieces of poled PZT ceramic without thermally depoling much of the ceramic, i.e., keeping the bulk of the material being joined below 300°C, while heating the joint region to about 1200°C for good bonding, the results were the production of a joint region about 10 µm in width with a heat-affected zone of only about 100 µm in width.

Coating Deposition and Removal. Another significant advantage of working at high frequencies is the ability to deposit significant amounts of energy into relatively thin material layers. This requires that: 1) the layer thickness is a significant portion of the wavelength in the material, and 2) that the material is at least somewhat lossy. For example, when the dielectric constant, ε, is about 10, as in alumina, the wavelength, at 83 GHz, in the material is about 1 mm, permitting heating of coatings <<1 mm thick For ε about 100, as with radar absorbing coatings, the wavelength in the material is about 0.4 mm, permitting significant heating of very thin coatings, if sufficient loss is present. We have explored the use of the 83 GHz system for both application and densification of coatings, as with ceramics coatings on metal substrates, and in removal of coatings. The latter, that was quite successful, as shown in Fig. 4, is the subject of a patent application [12] of use of a rastered millimeter-wave beam to remove radar-absorbing coatings from both metallic and composite substrates, replacing paint strippers and abrasive grit blasting as presently used. Both theoretical calculation and experiments show that we can heat a thin RAM coating to temperatures sufficient to remove it, while heating an aluminum or composite substrate to much less than 100°C.

Summary and Conclusions

The authors have demonstrated the successful use of microwave and millimeter-wave systems in several material processes. These systems can clearly be useful when very rapid thermal processing is required, as in obtaining ultra fine grain size solids from nanophase precursors. We have also demonstrated the use of the millimeter-wave beam system in joining high temperature ceramics, where the millimeter-wave approach has unique advantages over conventional methods—rapid thermal processing and controlled localized energy deposition. The millimeter-wave system is also potentially useful in removing certain types of coatings from metallic or composite
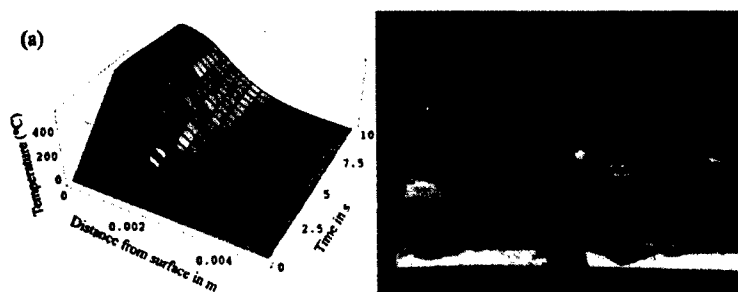
Fig. 4. (a) Theoretical calculation of energy deposition in 1 mm thick RAM coating on 5 mm thick FRP substrate and (b) removal of RAM coating with short 83 GHz pulse (700 J/cm^2)

substrates in an environmentally benign manner and without damage to the substrate. Finally, we have shown the potential for continuous, low cost production of nanophase materials–metals, metal oxides, mixtures of these, in a 2.45 GHz S-Band microwave waveguide system; this use could make much more practical the application of nanophase precursors in various materials and processes.

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