# **TECHNICAL INSIGHTS**

# ADVANCED MANUFACTURING





- 1. ALTERING THERMAL CONDUCTIVITY OF LEAD ZIRCONATE TITANATE
- 2. ENHANCEMENTS IN SURFACE ENHANCED RAMAN SPECTROSCOPY
- 3. ULTRA-MINIATURE GAS CHROMATOGRAPH TO DETECT VOLATILE ORGANIC COMPOUNDS
- 4. PATENT ANALYSIS OF BRAZING PROCESS
- 5. TECHVISION 2015

#### **1. ALTERING THERMAL CONDUCTIVITY OF LEAD ZIRCONATE TITANATE**

Lead zirconate titanate (PZT) is a widely used type of piezoelectric material used in sensors, such as ultrasonic sensors; sensors to detect flow, vibration or load; tactile sensors and so on. When deformed, a piezoelectric material generates an electric charge. Conversely, when an electric field is applied to a piezoelectric material, the material undergoes deformation.

The ability of lead zirconate titanate to produce an electrical charge when mechanically compressed or to vibrate when an electrical charge is applied renders such material highly conducive for passive sensing, active transmitting, or mechanical displacement applications.

Hard, high-power piezoelectric materials are ceramic-type materials capable of withstanding high levels of electrical and mechanical stress. Such materials are especially suited to high voltage or high power applications.

Soft, high-sensitivity piezoelectric materials are especially suitable for sensing applications owing to their high sensitivity and permittivity. Such piezoelectric ceramic materials are used in low-power applications, such as sensors, receivers, or transmitters.

Additional attributes of PZT include: wide range of frequencies, high output, high frequency, fast response time, high sensitivity, and so on. Applications for PZT-based sensors include, for example, flow sensors, level sensors, ultrasonic sensing (including non-destructive evaluation).

Traditionally, it has not been possible to alter a material's thermal conductivity at room temperature. This limitation has impeded the creation of

new, enhanced devices that use phonons, as opposed to electrons or photons, to transmit information or harvest energy. Phonons, which can transport heat energy in solids up to the speed of sound, have been difficult to harness.

Using only a 9-volt battery at room temperature, a team, led by Sandia National Laboratories researcher Jon Ihlefeld, has succeeded in altering the thermal conductivity of PZT (lead zirconate titanate) by as much as 11% at subsecond time scales. This feat was accomplished without having to change the material's composition or forcing phase transitions to other states of matter. In addition to researchers from Sandia National Laboratories, the team included researchers from the University of Virginia and Penn State University.

The researchers were able to alter the thermal conductivity of PZT over a wide temperature range rather than only at cryogenic temperatures. Furthermore, the technique is reversible. The thermal conductivity returns to its original value when the voltage is released.

The use of materials with domain walls (closely spaced internal surfaces) allowed for improved control over the passage of the phonons.

The researchers advanced the field of phononics by preparing crystalline materials with interfaces that are able to be altered by an electric field. Since the interfaces scatter phonons, the researchers are able to actively alter a material's thermal conductivity by changing their concentration.

The researchers used a scanning electron microscope and an atomic force microscope to study how the domain walls of the material's subsections changed in length and shape in the presence of an electrical voltage, a change that controllably altered the transport of phonons within the material. This research has been supported by Sandia's Laboratory Directed Research and Development office, the US Air Force Office of Scientific Research, and the National Science Foundation,

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#### 2. ENHANCEMENTS IN SURFACE ENHANCED RAMAN SPECTROSCOPY

Raman spectroscopy relies on inelastic scattering, or Raman scattering, of light to identify molecule and provide information about molecular vibration, which can be used for identification and quantitation of a sample. It entails shining monochromatic light from a source such as a laser on a sample and detecting the scattered light. Most of the scattered light is of the same frequency as that of the excitation source, which is known as Raleigh or elastic scattering.

Raman scattering is a spectroscopic technique that is complementary to infrared absorption spectroscopy. Raman scattering can provide certain advantages compared to mid-IR and near-IR spectroscopy, such as minimal or no sample preparation is required; Raman bands can be readily related to chemical structure; Raman spectral bands are narrower than mid-IR spectra and combination bands are usually weak; the spectral range is suitable for both organic and inorganic species, and special accessories are not required to measure aqueous solutions.

Surface Enhanced Raman Spectroscopy (SERS) is a Raman spectroscopic technique that provides a considerably enhanced Raman signal from Ramanactive analyte molecules adsorbed onto certain prepared metal surfaces. SERS can offer molecular fingerprint specificity along with potential single-molecule sensitivity. Therefore, it can be attractive tool for sensing trace amounts of molecules for chemical and biochemical analysis.

Despite its high specificity and sensitivity, SERS has thus far not been significantly commercially established, due to such factors as the low reproducibility of the SERS signal and the expensiveness and fabrication difficulty of the materials used in the SERS technique.

A team, led by researchers at The State University of New York at Buffalo, has been developing an innovative universal SERS substrate that could results in a more streamlined, less expensive SERS technique. The SERS substrate can allow for detecting and measuring chemical and biological molecules by employing a nanostructure that collects a wide range of light transmissions.

The conventional SERS technique enhances the Raman signal and scattering intensity by using a nanopatterned substrate. Such substrates, however, often are designed only for a narrow range of wavelengths and, therefore, are not very suitable or efficient for use with different laser light sources. The researchers have designed a universal substrate that is able to trap a wide range of wavelengths and implement the wavelengths in tiny gaps for an enhanced light wavelength capability.

The technology created by the researchers includes a thin film of silver or aluminum that serves as a mirror, and a dielectric layer of silica or alumina. The dielectric material separates the mirror with minute metal nanoparticles located at the top of the substrate.

The SERS technique, which can enable detection of tiny chemical or biological molecules, could have opportunities in applications such as biosensors for disease detection, detecting art forgeries or restoring old artwork (by detecting chemicals in the paint), detection of trace amounts of pollutants or detecting chemical weapons.

The research was supported by The National Science Foundation to develop a real-time in vivo biosensing system.

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### 3. ULTRA-MINIATURE GAS CHROMATOGRAPH TO DETECT VOLATILE ORGANIC COMPOUNDS

Gas chromatographs use analytical separation techniques to analyze volatile substances in the gas phase by separating the analytes in the sample. The components of the sample are dissolved in a solvent and vaporized to separate the analytes. The sample is distributed between two phases—a stationary phase and a mobile phase. The mobile phase entails a chemically inert carrier gas, such as helium, or an unreactive gas such as nitrogen, that carries the molecules of the analyte through the heated column. Gas chromatography does not use the mobile phase for interacting with the analyte. The stationary phase involves either a solid adsorbant, called gas-solid chromatography (GSC), or a liquid on an inert support, called gas-liquid chromatography (GLC).

The gaseous compounds under analysis interact with the walls of a column, coated with a stationary phase. This phenomenon causes each compound to elute at a different time. The useful of the GC relates to the retention times of the different compounds.

Gas chromatographs have historically been bulky, cumbersome instruments. Microfabricated gas chromatographs, on the other hand, can allow for key benefits in gas chromatography, such as smaller size, lower power, faster analysis time, and reduced cost. Gas chromatographs are, moreover, used to separate and analyze volatile organic compounds (VOCs) in gases (or liquids or solids).

Masoud Agah of Virginia Tech and his graduate students have been advancing the miniaturization of gas chromatographs by developing a credit-cardsized gas chromatography platform capable of analyzing volatile compounds within seconds. Such miniaturized systems can provide portability for analysis in remote settings along with high throughput and reduced cost.

Agah has noted that the hybrid integrated approach for developing a micro gas chromatograph allows key components of the system to be miniaturized individually on chips that are fabricated separately. This is followed by manual assembling of these components by using commercially available off-chip fluidic interconnects. The hybrid integration scheme can increase fabrication cost because the components are processed separately. Manual assembly of the individual components can be time-consuming, difficult, and increase the micro chromatograph system's weight and footprint.

In contrast, single chip or monolithic integration of the micro chromatograph components can yield additional advancements in size, cost, and performance.

Agah and his students have developed a gas chromatography-on-chip module that can provide very efficient separations and detection, reduced analysis time using temperature and flow programming, and rapid detection suitable for high-speed gas chomatography. The system has also shown high repeatability (less than 10% variations), with no observed deterioration of the detector excitation electrodes after being operated continuously for 12 hours.

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#### **4. PATENT ANALYSIS OF BRAZING PROCESS**

Brazing is a type of joining method where the merging of the two parts consisting of different materials is done by heating them to a suitable temperature. A filler metal, an essential part of the brazing process, has a liquidus temperature of above 4270 degrees C; and this temperature needs to be below the solidus temperature of the base metal. The fillers used in this process are usually non-ferrous metals or alloys and these filler metals are evenly distributed throughout the mated parts that are to be fitted and joined. In the brazing process, it is not necessary to melt the base metal; instead, the filler metals with low melting point are employed against the base metal. In this joining process, the base metals are cleaned to remove the impurities such as oxides, oils, and so on. The filler metal is then used to wet the surface of the base metal and it is spread along the consecutive joint. In order to further aid the brazing process, fluxes are additionally employed to increase the wet properties of the base metal surface. The capillary attraction between the filler and the base metal is significantly higher than that between the flux and base metal. Fluxes used in this process help in making the filler metals flow into the minute gap of the parts that are to be joined together. The advantages of the brazing process are that this process can be employed for a large number of dissimilar metals and the resulting parts can be of a wide range of thicknesses. The other advantages are that complex and multi component assemblies can be joined in an economical way and the strength of the joints obtained is also very high.

From the patents exhibited below it can be seen that a number of companies, such as General Electric Company, GM Global Technology Operations LLC, Ceramic Fuel Cells Limited, Aegis Technology Inc, have been working on improving the brazing process (including the braze material), which can increase the overall output of the material that has been joined using the brazing process.

For example, Patent # US 20130095342 A1, assigned to General Electric Company, pertains to a brazing process, braze assembly, and braze article The process includes applying the blaze material to an article within a vacuum chamber while the chamber is evacuated.

Title	Publication Date/Publication Number	Assignee	Inventor	Abstract
Brazing process, braze assembly, and brazed article	October 14, 2011/ US 20130095342 A1	General Electric Company	David Edward Schick, Dean William MORRISON, Srikanth Chandrudu Kottilingam, Yan Cui, Brian Lee Tollison, Dechao Lin	A brazing process, a braze assembly, and a brazed article are disclosed. The brazing process includes applying a braze material to an article within a vacuum chamber while the vacuum chamber is substantially evacuated. The braze assembly is capable of applying a braze material to an article within a vacuum chamber while the vacuum chamber is substantially evacuated. The brazed article is devoid of re-formed oxides.
Rotor for electric motor and brazing process	August 15, 2011/ US 20130043760A1	GM Global Technology Operations LLC	Richard J. Osborne, Qigui Wang, Yucong Wang	A plurality of conductor bars are positioned within slots of a laminated electric steel disc stack, and the ends of the conductor bars are brazed to end rings to manufacture a rotor. The method includes inserting the conductor bars into the slots of the disc stack, providing the end rings with slots for receiving the ends of the conductor bars; positioning spacers of braze material adjacent each end of each of the conductor bars to create a gap between the end rings and the steel disc stack; and applying heat to melt the braze material of the spacers whereby braze material is furnished by the spacers of braze material to braze the first and second ends of the conductor bars to the first and second end rings. Channels are provided in the face of the end rings facing the steel disc stack to drain away excess braze material.
Brazing process	July 10, 2010/ US 20120225306A1	Ceramic Fuel Cells Limited	PaulZheng	A brazing process for joining at least two components having ceramic oxide surfaces is described. The brazing filler used in the process comprises a noble metal and a second metal. During the brazing process, the filler is heated in an oxidising atmosphere such as air. The heating is undertaken until at least the noble metal is molten. The molten filler comprises a surface oxide formed from a stable, non-volutile oxide of the second metal that does not significantly alloy with the molten noble metal. The molten filler is able to wet the ceramic oxide surfaces and is subsequently cooled between them to thereby join them together.
Innovative braze and brazing process for hermetic sealing between ceramic and metal components in a high-temperature oxidizing or reducing atmosphere	April 19, 2010/ US 8511535 B1	Aegis TechnologyInc	Quan Yang, Chunhu Tan, Zhigang Lin	A superior braze material, along with a method of producing the braze material and a method of sealing, joining or bonding materials through brazing is disclosed. The braze material is based on a metal oxide-noble metal mixture, typically Ag—CuO, with the addition of a small amount of metal oxide and/or metal such as TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , YSZ, Al, and Pd that will further improve wettability and joint strength. Braze filer materials, typically either in the form of paste or thin foil, may be prepared by a high-energy cryogenic ball milling process. This process allows the braze material to form at a finer size, thereby allowing more evenly dispersed braze particles in the resultant braze layer between on the surface of the ceramic substrate and metallic parts.

Title	Publication Date/Publication Number	Assignee	Inventor	Abstract
Vacuum brazing process for honeycomb structure of heavy- duty combustion engine	December 23, 2009/ CN 102107307 B	Shenyang Liming Aero-Engine (Group) Co., Ltd.	Du Jing, Shen Qu, Kongqing Ji, Jin Ying, Yang Shuo, Zhang Lei	Heavy-duty gas turbine honeycomb structure vacuum brazing process method, material to be welded to one or a combination of the following: GH536, 1Cr18Ni9Ti, GH4708, K4104; brazing material is B-Ni73CrSiB-40Ni-S; brazing process parameters as: $(5 ~ 10) \degree C$ / min heating rate to (950 ~ 550) \degree C, heat (15 ~ 25) min; finally (5 ~ 10) \degree C / min heating rate to (950 ~ 1000) \degree C, heat (15 ~ 25) min; finally (5 ~ 10) \degree C / min heating rate to (950 ~ 1000) \degree C, heat (110 ~ 20) min brazing; welding followed by furnace cooling to 1000 ° C after rapid cooling, the sample is cooled to below 100 ° C baked. The invention has strong operability, technology and good effect, with great economic value and technical value.
Process for fluxless brazing of aluminium and brazing sheet for use therein	November 04, 2009/ EP 2382087 A1	Aleris Aluminum Koblenz GmbH	Adrianus Jacobus Wittebrood	The invention relates to a process for controlled atmosphere brazing comprising, brazing an aluminium alloy without flux in a controlled atmosphere, while using brazing sheet comprising of an aluminium alloy core upon which on at least one side a layer of filler alloy is clad, the filler clad layer having an inner-surface and an outer-surface, the inner-surface is facing the core and the outer-surface is devoid of any further metallic based layers, and wherein the filler alloy has a composition which is Na-free, Li-free, K-free, and Ca-free, and comprising, in wt %: Si 3% to 15%, Mg 0.05% to 0.5%, one or more elements selected from the group consisting of (Bi 0.03% to 0.2%, Pb 0.03% to 0.2%, Sb 0.03% to 0.2%, and the sum of these elements being 0.2% or less), Fe 0 to 0.6%, Mn 0 to 1.5%, the balance aluminium and incidental impurities.
Microwave brazing process	November 27, 2007/ EP 1927420A3	General Electric Company	David E. Budinger	A process for heating a braze alloy by microwave radiation (26) so that heating of the alloy is selective and sufficient to cause complete melting of the alloy and permit metallurgical bonding to a substrate (14) on which the alloy is melted, but without excessively heating the substrate (14) so as not to degrade the properties of the substrate (14). The process entails providing metallic powder particles (12) having essentially the same metallic composition, with at least some of the particles (12) being sufficiently small to be highly susceptible to microwave radiation (26). A mass (10) of the particles (12) is then applied to a surface of a substrate (14), after which the mass (10) is subjected to microwave radiation (26) so that the particles (12) within the miass (10) couple with the microwave radiation (26) and sufficiently melt to metallurgically bond to the substrate (14). The microwave radiation (26) is then interrupted and the mass (10) is allowed to cool, solidify, and form a solid brazement.

Title	Publication Date/Publication Number	Assignee	Inventor	Abstract
Microwave brazing process for forming coatings	December 15, 2006/ US 8574686 B2	General Electric Company	Laurent Cretegny, Daniel Joseph Lewis, Jeffrey Reid Thyssen	A process for forming a coating on a surface of a substrate, so that heating of the coating material and permit bonding to the substrate without excessively heating the substrate so as not to significantly degrade its properties. The process generally entails forming a brazing paste containing powder particles dispersed in a binder. The particles are formed of a composition that is susceptible to microwave radiation. The brazing paste is then applied to the surface of the substrate and subjected to microwave radiation so that the particles couple with the microwave radiation and are sufficiently heated to burn off the binder and then at least partially molten layer on the substrate. The microwave radiation is then interrupted to allow the at least partially molten layer on the substrate.
Two tier brazing process for joining copper tubes to a fitting	April 6, 2005/ EP 1584398 B1	United Technologies Corporation	Stephen L. Mayers	The invention relates in general to joining copper or copper alloy tubes to metallic tubes such as manifolds, and more specifically to a two step brazing method for joining such tubes and manifolds according to the preamble of claim 1. A brazing method of this kind is disclosed in JP 2001 087 853.
Method and arrangementfor a martensite-free brazing process	May 13, 2002/ CA 2385985C	Safetrack Baavhammar Ab, Ola Pettersen	Ola Pettersen	An apparatus for brazing a connecting piece of electrically conducting material such as metal, to a metal surface by means of a new type of temperature- controlled brazing whereby for certain types of material a brazing is obtained that is free of martensite formation underneath the brazed joint in, for example, railway track and/or pipework. The apparatus has an electrode and processing circuitry by which a voltage applied in electrical circuit with the electrode causes an electric arc to be struck between the electrode and an adjacent workpiece to generate the heat necessary for brazing.

#### Exhibit 1 depicts patents related to brazing process.

Picture Credit: Frost & Sullivan

#### 5. TECHVISION 2015

The TechVision program is the premier offering of Technical Insights, the global technology innovation-, disruption-, and convergence-focused practice of Frost & Sullivan. TechVision embodies a very selective collection of emerging and disruptive technologies that will shape our world in the near future. This body of work is a culmination of thousands of hours of focused effort put in by over 60 global technology analysts based in six continents.

A unique feature of the TechVision program is an annual selection of 50 technologies that are driving visionary innovation and stimulating global growth. The selected technologies are spread across nine Technology Clusters that represent the bulk of R&D and innovation activity today. Each Cluster represents a unique group of game-changing and disruptive technologies that attract huge investments, demonstrate cutting-edge developments, and drive the creation of new products and services through convergence.

Our technology analysts regularly collect deep-dive intelligence on several emerging and disruptive technologies and innovations from around the globe. Interviews are conducted every day with innovators, technology developers, funders, and others who are a part of various technology ecosystems. The respondents are spread across public and private sectors, universities, research institutions, and government R&D agencies. Each technology is rated and compared across several parameters, such as global R&D footprint, year of impact, global IP patenting activity, private and public funding, current and emerging applications, potential adoption rate, market potential, and so on. This organic and continuous research effort spread across several technologies, regions, organizations, applications, and industries is used to generate an annual list of Top 50 technologies that have the maximum potential to spawn innovative products, services, and business models.

Furthermore, we analyse several possible convergence scenarios where two or more of the Top 50 technologies can potentially come together to disrupt, collapse, and transform the status quo. Driven by IP interactivity emanating from each of the top technologies, a whole range of innovative business models, products, and services will be launched at unprecedented speed in the future. We have come up with over 25 such unique convergence scenarios.

The Top 50 technologies we have selected for TechVision 2015 have the power to drive unique convergence and catalyse wide-scale industry disruptions. Frost and Sullivan's TechVision program empowers you with ideas and strategies to leverage the innovations and disruptive technologies that can drive the transformational growth of your organization.

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