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Laser-Assisted Microwave Plasma Processing of Ceramic Coatings

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Abstract

The aim of Laser-Assisted Microwave Plasma Processing of materials, abbreviated as LAMPP, is to utilize a spatially well-confined laser beam to ignite and localize a microwave plasma plume as an energy source for the sintering, melting or recrystallization of ceramic coatings. The energy required for the high-temperature treatment is supplied to a significant extent from the microwave source that feeds the plasma while the laser beam is used to scan the microwave plasma over the surface area to be treated. The phenomena underlying ignition and sustainment of the plasma are described in respect of the two possible ignition mechanisms: Laser-Induced Breakdown, LIB, or Microwave-Induced Breakdown, MIB. The influence of the material to be processed on prevalence of one of these ignition mechanisms is discussed. Examples of equipment built in our laboratory to enable LAMPP in different atmospheres for different substrates and coatings are shown. As potential applications of LAMPP, re-melting of ceramic plasma-sprayed thermal barrier coatings and melting of non-stabilized ZrO_2 ceramic for coating purposes are presented.

Keywords: Microwave plasma, ceramic melt processing, LIB, MIB

I. Introduction

High-frequency coherent radiation sources for material processing are becoming increasingly important for the development of novel manufacturing technology, e.g. additive manufacturing, and for the improvement of coating processes, e.g. cladding. Lasers are widely used for processing metals and organic polymers, but they are less suitable for ceramic processing owing to an unfavorable combination of process parameters and material properties: a very high temperature is needed to activate diffusion or achieve melting while the resistance of ceramics to thermal shock is low, therefore fast heating of a ceramic part should be avoided. On laser treatment of ceramics, the energy intake rate is faster than heat dissipation, thus ablation of material occurs easily. Therefore laser processing of ceramics is better suited for cutting, milling, marking or drilling of ceramics rather than for sintering or melting [1].

Besides direct laser heating, ignition of plasma within the ablated and evaporated volume might occur. In this case the high laser irradiance required for heating ceramics must match the volume and composition of the ablated mass with regard to sufficiently fast diffusion of heat and mass from the ablated volume into non-shielding gaseous plasma, which actually absorbs the laser radiation and enables a continuous process [2]. The efficiency of laser energy utilization is in this case governed by the ablated material and the properties of the plasma which is highly confined by the laser beam [3]. Depending on the wavelength of the laser light and the pulse duration, either "plasma-mediated ablation" or "direct ablation by multi-photon absorption" dominates the laser-ceramic interaction [4]. However, in order to enable large-surface-area ceramic treatment for sintering, cladding or surface re-melting, ablation needs to be avoided.

We were therefore interested in the development of an alternative heating method based on additional coherent electromagnetic radiation sources, e.g. microwave sources, to achieve decoupling of material ablation from plasma formation and sustainment. Such decoupling became possible with the utilization of laser-assisted microwave processing [5]. In microwave radiation, photons carry a very low amount of energy, in the order of μeV, corresponding to 0.9 – 5 GHz frequency. Thus, direct ablation by means of microwave multi-phonon absorption can be excluded as a mechanism of ceramic-microwave radiation interaction. However, if the microwave energy is absorbed by a plasma plume, then plasma-mediated ablation can occur.

The unique feature of microwave plasma is the non-Maxwellian energy distribution at higher pressure [6]. It can therefore be utilized as weakly non-thermal "hot" plasma and serve as a source of thermal energy as well as a source of electrons with a "non-thermal" energy distribution. Such ambient pressure plasma is easily ignited and sustained using, for example, commercially available 2.45 GHz microwave radiation sources. The microwave plasma delivers to a substrate thermal energy as well as electrons, activated atoms, radicals or ions to initiate chemical reactions. Therefore microwave plasma has become a very powerful tool mainly for chemical vapor decomposition of precursors. Synthesis of ceramic coatings, e.g. diamond or non-oxide ceramic multilayer hard-coatings, with the help of microwave plasma-assisted chemical vapor deposition, CVD, was quickly adopted into industrial use [7].

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Processing of powder-based coatings with microwave radiation and microwave plasma as the single energy source has not been successful so far, mainly because focusing of the microwave electromagnetic field into a beam with a sufficiently high energy density is quite difficult, at least with easily accessible magnetron-based microwave sources. In addition, process control is an issue because the temperature dependence of microwave absorption is very pronounced: selective heating occurs in hot areas of a substrate with almost no absorption in cold areas. Unlike microwave sources, laser sources offer highly focused energy beams which can easily be scanned over the surface of a sample. Nevertheless, other problems, like e.g. bubble formation have to be overcome as shown in a recent publication on selective laser sintering of glass-ceramic powder [8]. Although a sufficiently high energy supply is obtained from a YAG-laser to sinter e.g. commercial lithium alumo-silicate Li_2O-Al_2O_3-SiO_2 glass tapes, a rather large amount of liquid phase is needed for promoting densification. The material obtained from this process is amorphous [8].

The first variant of Laser-Assisted Microwave Processing (LAMP) of materials [9] was based on plasma ignition due to a "hot-spot" formation by means of selective microwave heating of a ceramic: the process starts with a microwave-induced breakdown, MIB, as described in the following section. On the other hand, in analytical chemistry laser-induced breakdown, LIB, is applied for detection of elements with the help of optical emission spectroscopy. Recently, a combined method which utilizes LIB and microwave radiation has been developed with the aim of improving the LIB signal intensity [10]. Similar to LAMP, enhancement of the laser plasma with the help of simultaneous microwave irradiation has been investigated. Upon Microwave-Assisted Laser Induced Breakdown, MA-LIB, at low laser power, a significant enhancement of intensity of optical emission signals is observed for e.g. Al_2O_3 ceramics, which supports the concept of energy intake from the microwave field into plasma ignited by LIB [10].

Both areas of combined utilization of laser and microwave radiation are based on the presence of plasma. In order to emphasize the major contribution of plasma the acronym coined almost 14 years ago [9] will now be adjusted to *Laser-Assisted Microwave Plasma Processing*, LAMPP. The core development of LAMPP is the confinement and spatial control over the microwave plasma, which is guided by a weak laser beam and scanned over the surface of the material to be coated. The development goal is to suppress ablation and enable efficient heating of the microwave plasma at ambient pressure (~ 1 atm). Under such conditions, high-energy UV-photons in addition to thermal and non-thermal photons can be generated [11], which could further activate the surface-near region of the material and provide additional activation energy for diffusion, and for sintering and melting to obtain a powder-derived dense ceramic coating.

(1) Laser and microwave plasma generation and sustainment

Plasma can be seen as "gaseous electrolyte", containing an equal number of positively and negatively charged species and therefore overall electrically neutral. Unlike, for example, an aqueous electrolyte, which is electrically conducting owing to the presence of ions, gas plasma contains free electrons as negatively charged particles together with positively charged ions. With sufficiently high density of electrons in the plasma, an electromagnetic field will be reflected from the plasma plume, thus no energy from the external electromagnetic field can be coupled into the plasma.

If the density of electrons is reduced and their collision frequency approaches the frequency of an externally applied electromagnetic field (e.g. microwave field with GHz frequency or laser field with THz frequency), then acceleration of electrons in the plasma can occur: the plasma is heated by the external electromagnetic radiation.

For microwave radiation a critical electron density $N_{e,cr}$ of around $10^{11}\,cm^{-3}$, e.g. $7 \cdot 10^{10}\,cm^{-3}$ for radiation at 2.45 GHz is required for energy absorption and plasma heating. This low density does not exist in the core of an originally much denser laser-induced breakdown, LIB-plasma, which initially has a high electron density (about $10^{17} - 10^{19}\,cm^{-3}$). In order to couple microwave radiation and heat the LIB-plasma, relaxation and expansion of the LIB-plasma plume must occur. Coupling of microwave radiation in its periphery with low electron density then becomes possible. This is the principle of MA-LIBS [10].

In the presence of a microwave field, besides emission of free electrons from a solid material, plasma ignition can also be achieved by lowering the breakdown strength of the gas surrounding a solid material by e.g. evaporation of ionizable atoms or molecules as well as by decreasing the number of neutral species due to localized heating which leads to gas expansion. Upon expansion of the hot gas, density of neutral molecules or atoms drops locally, thus breakdown strength is reduced [12]. In addition, if, for example, a metal oxide is dissociated into metal vapor and oxygen upon high-temperature evaporation, as described by Eqs. (1) and (2), breakdown strength of the gas phase close to a heated metal oxide surface is further reduced by the presence of metal atoms that are ionized into positively charged metal ions and electrons. As shown in Table 1, each metal oxide will show a characteristic temperature for the "low threshold" plasma ignition upon microwave heating of the oxide [14], which is reached as soon as ~ 10^{-8} bar partial pressure of metal atoms is present. In such conditions microwave-induced breakdown, MIB, will occur.

$$Me^{a+}O_{\frac{a}{2}solid} \rightarrow Me^{a+}O_{\frac{a}{2}vapor} \rightarrow aMe + \frac{a}{4}O_2 \qquad (1)$$

$$Me = A \qquad A \rightarrow A^+ + e^- \qquad (2)$$

The differences and the common features of LAMPP that originate from different properties of the materials exposed to both sources of electromagnetic radiation are shown in Fig. 1. While some metal oxides are electron emitters, others supply ionizable metal atoms to the environment, thus MIB or LIB occurs [13,14]. However, independent of the plasma ignition mechanism, the laser-confined microwave plasma is the energy source for ceramic surface treatment. The scan velocity of the laser, the laser power parameters and microwave power parameters must be carefully adjusted so as to prevent separation of the plasma plume from the surface of the solid material to be coated. Details of some methods that can be applied for LAMPP process development are described in [14].

Table 1: Decomposition behavior of metal oxides in inert gas and in air: characteristic temperature to yield 10^{-8} bar metal vapor pressure upon inert conditions, which is sufficient to cause "low threshold" microwave plasma ignition, data from [13]

Metal	neutral	at 0,2 bar O_2	T_{crlt} [°C]
	p(Me) [bar]	p(Me) [bar]	
Ni (NiO)	$3{,}15 \cdot 10^{-8}$	$8{,}82 \cdot 10^{-12}$	1200
Zn (ZnO)	$4{,}48 \cdot 10^{-8}$	$1{,}50 \cdot 10^{-11}$	850
Mg (MgO)	$3{,}25 \cdot 10^{-8}$	$9{,}28 \cdot 10^{-12}$	1450
Sn (SnO_2)	$4{,}58 \cdot 10^{-8}$	$1{,}05 \cdot 10^{-14}$	1210

A clear distinction between an MIB- or LIB-ignition of the plasma is not possible unless *in-situ* plasma diagnosis is included, e.g. optical emission and Raman spectroscopy of the gaseous phase to identify the excited atoms and molecules. This work is set to commence in the near future. Common plasma diagnostic tools cannot be used because of the high temperature radiating from the hot ceramic surface.

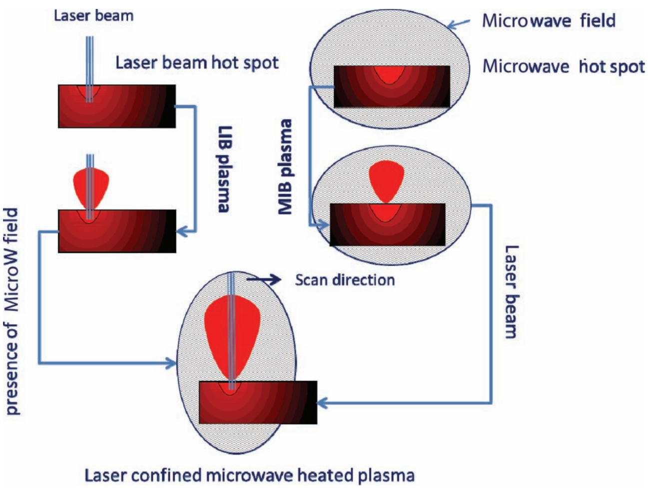

Fig. 1: Principle of LIB- and MIB-plasma ignition with LAMPP: a hot spot formed by selective heating either by a laser beam or a microwave field is the origin of plasma, which can be further heated by microwaves and confined and scanned with the help of a laser beam.

(2) Equipment for LAMPP

To the best knowledge of the authors, no standard equipment is available to perform LAMPP on ceramics for coating purposes. In the period 1998 – 2012, numerous variants of equipment were developed at the Chair of Materials Processing at the University of Bayreuth. Microwave processing can be performed in mono-mode or multi-mode cavities, details can be found in e.g. [15]. Similar, different lasers can be employed: cw or pulsed, with short or long wavelength of light. In order to identify the most important parameters for successful LAMPP, three different set-ups were developed and tested in our laboratory, as described below.

(a) *Mono-mode 2.45 GHz microwave cavity with cw-YAG laser*

The principle of this type of equipment is shown in Fig. 2. The mono-mode cavity is a rectangular waveguide with a length adjustable so as to have a defined maximum of electrical field strength at the position of the sample to be treated. Because microwave radiation is readily absorbed by semiconductors, e.g. SiC or ionic conductors, like Ca-YSZ, sample preheating is achieved by placing them on top of such a "microwave susceptor", which acts like a hot-plate. In this type of LAMPP system, ambient pressure and air are the atmosphere parameters. Upon plasma ignition the neutral molecules will be mainly nitrogen and oxygen. The YAG-laser radiation is coupled into the microwave cavity by means of a glass fiber system.

(b) *Graphite furnace as multi-mode 2.45 GHz microwave cavity with pulsed CO_2 laser*

In order to study the influence of pre-heating temperature and reduced pressure on LAMPP, a system was developed that enables external resistive heating of a graphite furnace up to 1500 °C and the application of vacuum. The graphite walls of the furnace serve as "resonator" for the microwave field. Coupling of microwave radiation proceeds via an antenna system developed for adding microwave heating to existing electrically heated furnaces without unreasonable heat loss [17]. In such a hot process chamber, fiber coupling of the laser beam is not practical, and therefore an optical system was developed. The laser radiation is coupled via an IR-transparent window into the hot process chamber. The principle of this type of LAMPP equipment is shown in Fig. 3 while a view of the real system is shown in Fig. 4.

(c) *Mono-mode 2.45 GHz microwave cavity with pulsed CO_2 laser*

The laser wavelength is crucial for LIB because most "white" ceramics do not absorb visible light sufficiently well. Therefore another mono-mode microwave cavity, a cylindrical one, was equipped with a CO_2-laser instead of the YAG-laser. The basic principle is similar to the system shown in Fig. 1. As an additional tool to better adjust and synchronize the microwave field with the laser beam movement, a cylindrical wave guide was chosen, because in this case the adjustment of the height of the cavity will enable matching of the electrical field maximum of the microwaves in a cavity filled with absorbing materials. The principle of this set-up is shown in Fig. 5.

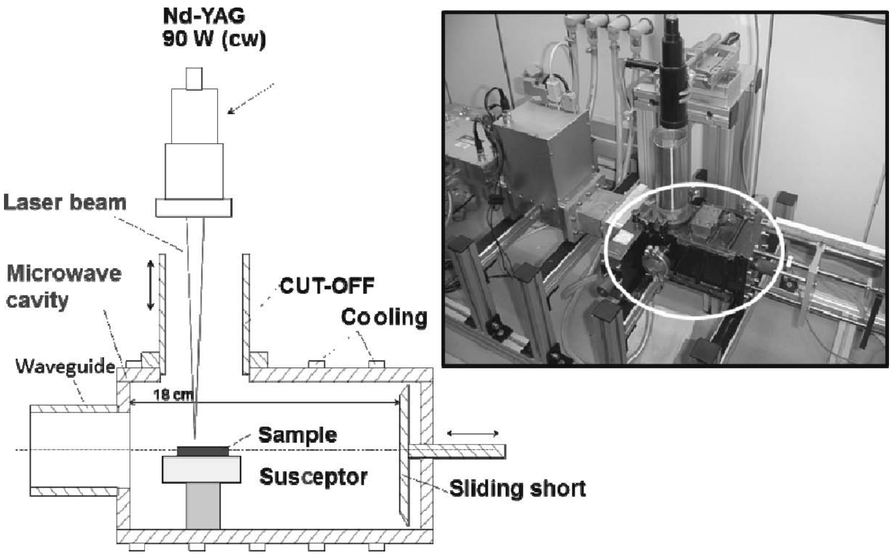

Fig. 2: LAMPP set-up for a YAG-laser coupling via fiber into a mono-mode microwave cavity.

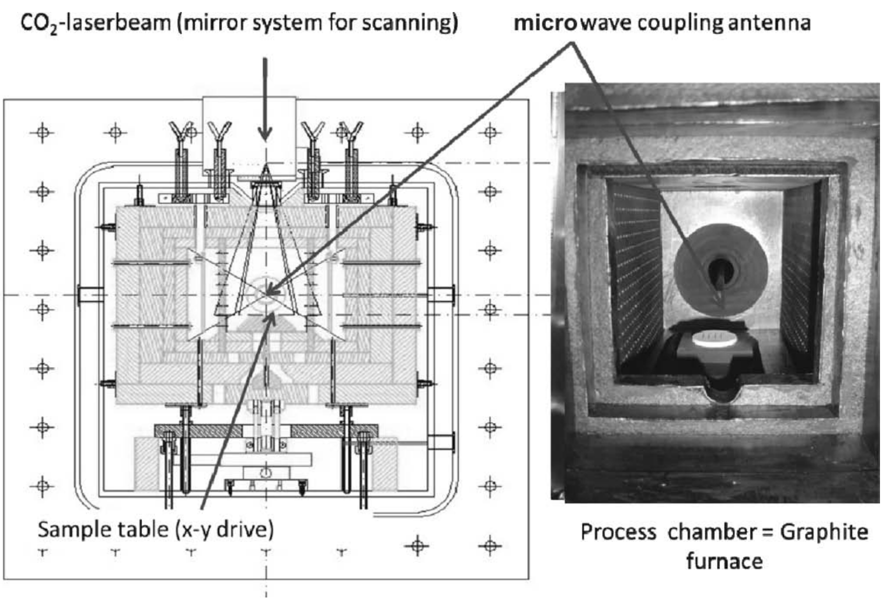

Fig. 3: LAMPP set-up for an optically (mirror system) coupled CO_2-laser into a multi-mode microwave cavity.

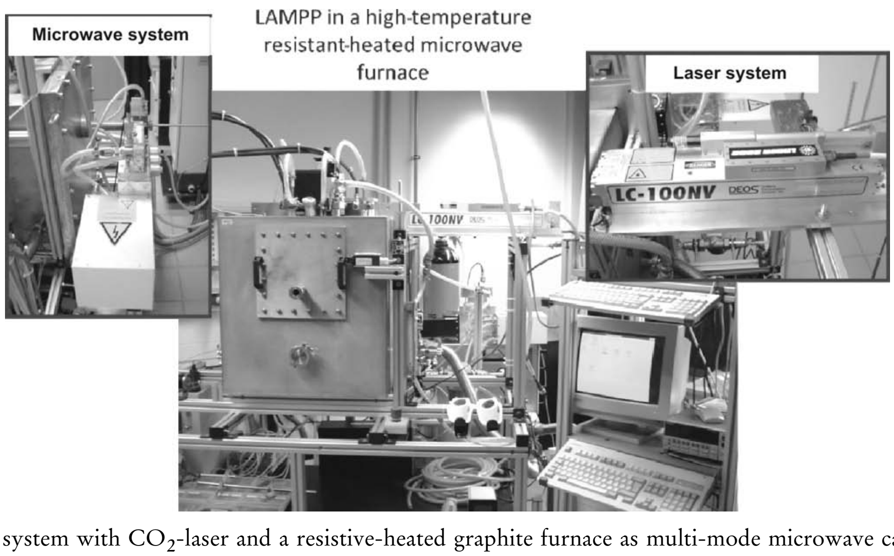

Fig. 4: View of the real system with CO_2-laser and a resistive-heated graphite furnace as multi-mode microwave cavity.

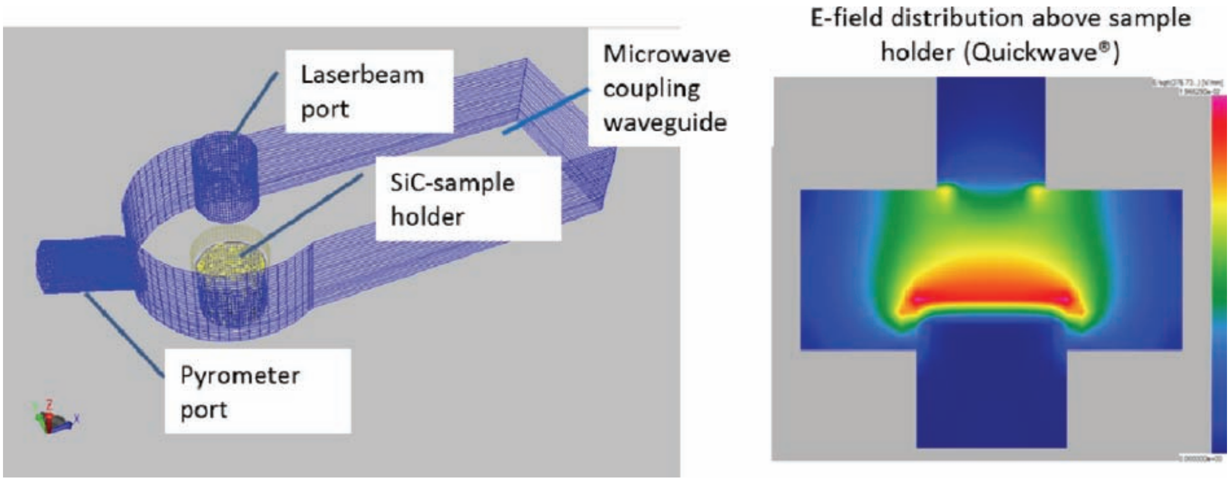

Fig. 5: Improved LAMPP system design based on simulation of the electromagnetic field distribution: E-field distribution above the sample holder in a cylindrical mono-mode microwave cavity.
Waveguide R26 (86 x 43 mm), Cavity Ø 100 mm, Height 43 mm
Sample holder SiC Ø 40 mm, h=10 mm ($\varepsilon' = 190$, $\sigma = 26.5$ S/m, $\varrho = 2.75$ g/cm³)
Frequency 2.45 GHz, Power 1 W (simulation; real ~200 – 400 W).

II. Experimental

Ceramic materials: 7Y-ZrO_2 TBCs on steel and Ni-SA (U of Dortmund, LS Werkstofftechnik, Germany); ethanol-water-based ceramic slurry: 20 wt% NiO/80 wt% $ZrSiO_4$, non-stabilized ZrO_2 powder (H.C. Starck), dense CT 800 Al_2O_3 ceramic.

Microwave and laser equipment: Microwave systems: Puls Plasma Technik 3 kW, 2.45 GHz; Homer Muegge MW-HMD 2450 – 2; Autotuner Muegge MW-ALM 2450 – 1;

Nd:YAG Laser Spectron SL 901, 90W (cw); DEOS RF excited LC-100NV OEM/

DEOS RF excited LC-100NV OEM/Industrial CO_2-laser, wavelength 10.6 µm, cw-power ~ 100 W, stability < ± 2 %, mode 95 % TEM00, beam size 3.8 ± 0.4 mm, divergence < 4 mrad, modulation: TTL up to 25 kHz.

Temperature measurement: Pyrometer Keller PZ20 AF1; T-range 200 – 1800 °C, applied in all LAMPP experiments. The pyrometer is focused on the sample surface and fixed with a large spot size above the center of the treated area. Radiation emitted from the plasma causes jumps in the temperature signal. The upper temperature limit is characteristic of the melt temperature, the lower limit of the non-molten substrate. The pyrometer spot covers a much larger area than the laser.

Typical LAMPP parameters: e.g. for 100 W CO_2 laser: 25 kHz, 10 µs Q width for RF train control, corresponding to laser output power > ~ 27 W, scan velocity 2 mm/s; 2 kW – 2.45 GHz microwave power, upon plasma ignition 0 % reflected power, then reduction of microwave power to 200 – 400 W to sustain the plasma. The LAMPP is accompanied by enormous acoustic emissions.

III. Results

(1) LAMPP in a mono-mode 2.45 GHz microwave cavity with cw-YAG laser

In Figs. 6 and 7 experimental proof of the microwave-induced breakdown plasma model (MIB) is shown for NiO-ZrO_2 eutectic ceramics [5]. Ni-oxide has a rather low temperature for the "low threshold" plasma ignition upon microwave heating. It is therefore difficult to heat oxides that easily decompose in the gas phase into metal vapor and oxygen with microwaves only without ignition of plasma [15]. Because of the high conductivity of the microwave plasma, a significant portion of the microwave radiation is reflected. Because of uncontrolled plasma ignition, some metal oxides, e.g. NiO, cannot be efficiently heated by absorption of microwave radiation up to their melting temperature even though a very high microwave power level is applied. The ignition of plasma is visible in Fig. 7 from the high noise level of the temperature reading recorded above the sample with a pyrometer.

Originally, these problems, which were observed upon attempts to use microwave heating for processing eutectic ceramic melts, were the starting point for development of LAMP [9, 14]. It could be shown that application of a weak Nd-YAG laser beam to a NiO-ZrO_2 sample heated with microwaves to approx. 1200 °C enables controlled and fast plasma ignition as well as stable plasma sustainment for further heating of the ceramic, as visible from a comparison of Figs. 4 and 5. With adjustment of the laser power and scan velocity, the plasma could be guided over the sample surface. Therefore LAMPP was employed to coat a dense ceramic 8Y-ZrO_2 substrate with a eutectic NiO-ZrO_2 melt to obtain microstructures electrodes for SOFC [5, 14].

Controlled microwave melting of ceramic powders on top of a ceramic substrate is divided into three steps: First, moderate heating occurs with medium power (< 500 W) up to a certain threshold temperature. This step is best described using the thermal runaway approach explained by Kenkre [16]. Once a hot area is developed by absorption of microwaves in a material with a positive temperature coefficient of dielectric loss, further microwave heating tends to become confined to this area – a hot spot is developed. On increase of the MW power (500 – 1000 W), the breakdown or "low threshold" plasma ignition is achieved by MIB and the heating mechanism is changed from volumetric to surface heating. Finally, in "Phase 3" holding the melting temperature with a low MW power of approx. 200 – 400 W is possible. The microwave power density at the surface is about 10^7 W/m^2, which is very near to low-power laser processing. In "Phase 3" of the heat treatment profile, shown in Fig. 4, smooth melting of the ceramic eutectic occurs, yielding upon cooling a eutectic Gd_2O_3-ZrO_2 or NiO-ZrO_2 ceramic with unique microstructure [14]. A typical appearance of such eutectic ceramics is shown in the SEM images in Fig. 8.

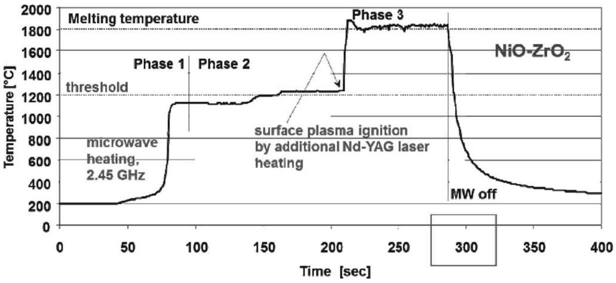

Fig. 6: Heating profile at the surface of a NiO-ZrO_2 dense ceramic body subjected to heating with microwaves (2.45 GHz) (Phase 1 and 2) followed by plasma heating initiated with an Nd-YAG laser: at 1200 °C, the "low threshold" condition for plasma ignition is reached.

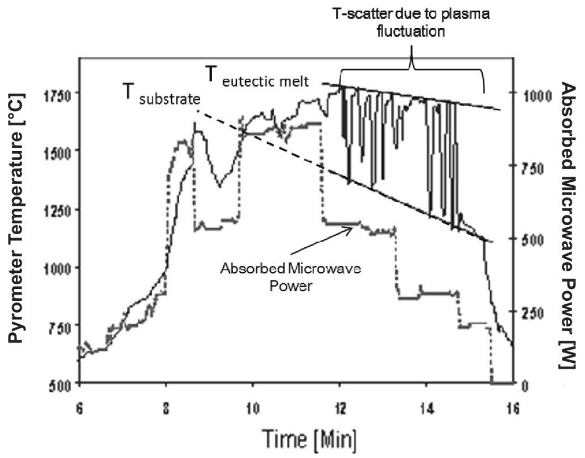

Fig. 7: Heating behavior of a NiO-ZrO_2 dense ceramic body subjected to heating with microwaves (2.45 GHz) only.

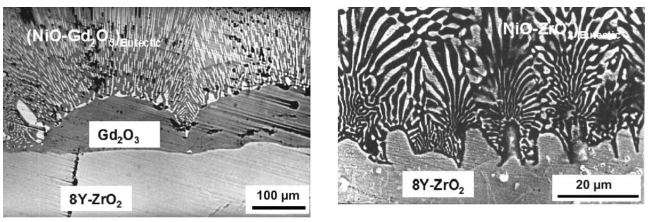

Fig. 8: YAG-cw-laser, mono-mode microwave cavity, ambient pressure, air CSZ-microwave susceptor pre-heating, ceramic melt coating starting from slip-cast powder, SEM images of eutectic ceramic melts deposited on top of dense zirconia substrates by means of laser-assisted microwave processing (see also [14]) followed by fast solidification: left NiO-Gd_2O_3-eutectic, right NiO-ZrO_2-eutectic.

The threshold temperature for microwave discharge (microwave-induced breakdown, MIB) could be confirmed experimentally for several oxides [14]; the data are summarized in Table 2. The vapor pressure of the oxides scales as follows: $p_{ZnO} > p_{NiO} \cong p_{SnO2} > p_{MgO} >>> p_{Y2O3}, p_{ZrO2}$. It could therefore be expected that pure ZrO_2 or Y_2O_3 ceramics would not spontaneously support microwave-induced breakdown, MIB, unlike ZnO, NiO and SnO_2, which would enable plasma ignition by MIB.

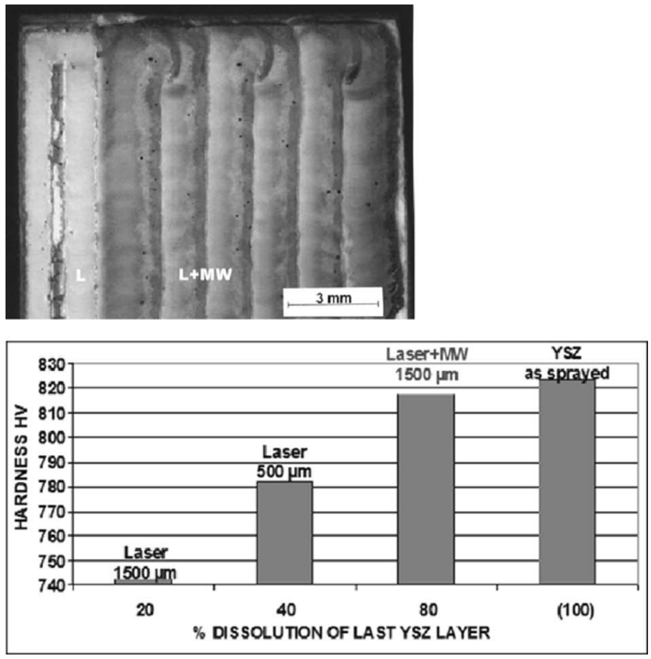

Fig. 9: YAG-cw-laser, mono-mode microwave cavity, ambient pressure, air SiC-microwave susceptor pre-heating and melting followed by solidification of an atmospheric-plasma (AP)-sprayed yttria-stabilized zirconia thermal barrier coating (YSZ-TBC); left side: light microscope image of the YST-TBC-coating processed by laser melting (L) and LAMP (L+MW); right side: corresponding hardness values of the coatings, data from [13]. Parameters: cw YAG 14 W, φ 500 µm, 250 W, 2.45 GHz, scan velocity < 3500 µm/sec.

Not only powder-derived ceramics can be sintered and melted but also a thermal barrier coating obtained by means of atmospheric plasma spraying (abbreviated as APS) from 8Y-ZrO_2, as shown in Fig. 9, can be sintered and fused together with an additional powder layer. The degree of heat intake is analyzed with the help of Vickers hardness measurements: the higher the hardness the more additional powder has dissolved in zirconia as a result of LAMPP heat treatment/melting [14]. The plasma-sprayed YSZ layer is taken as a reference. Tests with additional 20 %NiO-80 %$ZrSiO_4$ powder deposited on top of the TBC were performed, showing the potential of using LAMPP for the fabrication of environmental barrier coatings, EBC [14].

The microwave power needed to sustain the plasma upon MIB is ~ 200 – 250 W, much lower than the microwave power required for "dielectric" heating of the ceramic part, as clearly visible in Fig. 7. This shows impressively the high efficiency of microwave coupling into the plasma. It should be emphasized that independent of the treatment time with microwave plasma only a very small "hot spot" of a melt pool is formed at the surface of the ceramic [14]. This is caused by the selectivity of microwave heating: because dielectric loss increases with temperature, once a "hot spot" formed it will persist [16]. Only with the help of the YAG laser beam, which confines the microwave plasma and moves it away – when properly scanned – from the original "hot spot", could a larger area of a ceramic surface be melted and solidified to form a ceramic coating [5, 9, 14].

(2) LIB-based laser-assisted microwave processing

In the case of Al_2O_3 and SiO_2 ceramics, no clear conclusion could be drawn so far from experiments on MIB-based LAMPP using a YAG laser and a mono-mode microwave cavity because of the large scatter of data and limited number of experiments [14], as stated in Table 2. Therefore the influence of the pre-heating temperature of alumina ceramic on LAMPP was investigated with the help of the externally heated multi-mode microwave cavity and a CO_2 pulse laser. From previous work a critical temperature of 1650 – 1750 °C was found, as summarized in Table 2. Because such a high pre-heating temperature would not only be dangerous for the IR-transparent coupling window (chalcogenide glass, water-cooled flange only) but also exceed the sintering temperature of the Al_2O_3 samples, temperatures of ~ 0.2 and 0.6 $T_{melting}$ were applied for preheating. As shown in Fig. 10 and summarized in Table 3, first the laser parameters were varied while the microwave power was kept at < 1000 W. Because of the large multi-mode cavity, this microwave power was needed to accommodate heat loss to the water-cooled furnace walls and microwave coupling system. From SEM images of the laser-treated Al_2O_3 traces shown in Fig. 11, the major effect of the pre-heating temperature on cracking of the ceramic is visible. While at 400 °C pre-heating temperature, a crack-step-size of 200 μm is found this is increased to 400 μm at 1200 °C, thus a significant reduction in crack density is achieved. Further reduction in the depth of cracks is observed when the laser power is increased, as visible from the SEM images shown in Fig. 12.

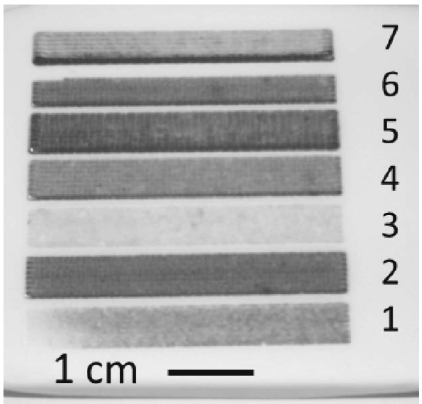

Fig. 10: LAMPP processing of dense Al_2O_3-ceramic with pulsed CO_2-laser, hot multi-mode cavity, ambient pressure, Ar, furnace temperature 1200 °C, microwave power < 1000 W; laser parameters see Table 3. Samples for parameter study.

Table 2: Critical temperature for microwave-induced plasma, MIB ignition at the surface of a microwave-heated oxide ceramic, as compared to melting temperature of the oxide (data from [13]); data for oxides without an index are calculated or taken from a database.

Oxide	ZnO*	CuO	NiO*	SnO_2*	CoO	SiO_2**	MgO*
T_{crlt}#[°C]	800 – 880	820 – 900	1150 – 1250	1150 – 1250	1200 – 1300	1370 – 1470	1400 – 1500
T_{melt}[°C]	1980	1326	1990	1630	2600	1710	2850
Oxide	$Ti0_2$	CaO	Al_2O_3**	Y_2O_3	$Zr0_2$	La_2O_3	HfO_2
T_{crlt}[°C]]	1560 – 1710	1580 – 1710	1650 – 1750	2040 – 2130	2220 – 2370	2240 – 2410	2350 – 2500
T_{melt}[°C]	1860	2930	2050	2410	2700	2310	2790

#: Temperature with a partial pressure of metal ~10^{-8} bar, sufficient for "low threshold" microwave discharge
*: critical temperature experimentally verified
**: critical temperature experimentally investigated but large scatter of data and only limited number of experiments

Table 3: LAMPP with CO_2-laser in a hot microwave multimode furnace to melt and crystallize the surface of dense Al_2O_3 ceramics; laser processing parameters.

N°	v [mm/s]	Frequency [kHz]	Pulse width [μs]	DF [%]	Spot distance [μm]	Line width [μm]
1	10	1	100	10	10	300
2	10	1	200	20	10	300
3	10	5	20	10	2	300
4	10	5	40	20	2	300
5	10	5	80	40	2	300
6	10	10	20	20	1	300
7	10	10	40	40	1	300

The same system was employed for processing of EBC (environmental barrier coatings) based on a high-melting Yb_2SiO_5 powder on top of a porous Si_3N_4-Yb_2SiO_5 ceramic [18]. The powder slurry is cast on top of a porous ceramic. Selective laser sintering (abbreviated as SLS) is performed on preheated samples with a CO_2 laser and compared with LAMPP. As can be seen in the upper part of Fig. 13 from the SEM side-view of the LAMPP-treated sample, melting has occurred. This is supported by comparison of the smooth surface appearance of LAMPP sample shown in the upper part of Fig. 13 with the rough surface of a sample sintered at 1650 °C for 50 h, which is shown in the bottom part of Fig. 13. SLS is not capable of melting the powder. Because the melting temperature is ~ 1950 °C, the heat loss by radiation from the surface is enormous, thus only hot plasma that reduces heat loss from the surface delivers enough energy for sintering and possibly even partial melting of Yb_2SiO_5.

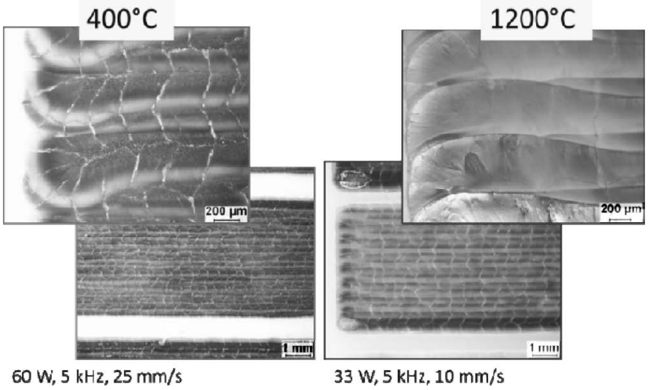

Fig. 11: Influence of pre-heating temperature on crack formation; laser parameters left side of figure: 60 W, 5 kHz, 25 mm/s; right side of figure: 33 W, 5 kHz, 10 mm/s.

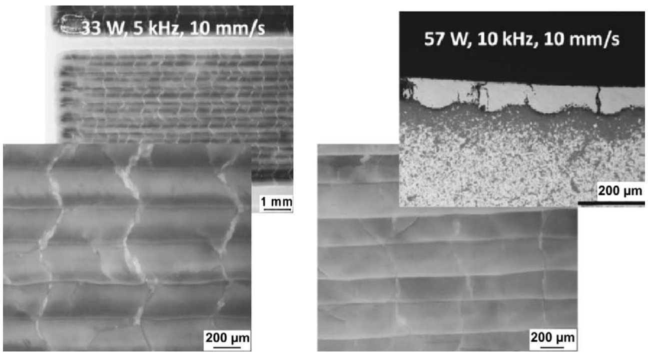

Fig. 12: Influence of laser pulse parameters on coating morphology at 1200 °C pre-heating temperature; laser parameters left side of figure: 33 W, 5 kHz, 10 mm/s; right side of figure: 57 W, 10 kHz, 10 mm/s.

Finally, pure zirconia coatings were investigated. As described in the previous section, oxides like, for example, ZrO_2 and Y_2O_3 are not suitable for MIB-based LAMPP because of the very low tendency of these oxides to evaporate. On the other hand, such oxides act as electron emitters at elevated temperature [13]. Therefore plasma ignition can be achieved with the help of LIB instead of MIB. For LIB-based LAMPP, a pulsed CO_2 laser with a maximum CW power of 100 W is used (gravure laser). The plasma is guided by the laser but powered by absorption of microwave radiation. The heating profile is shown in Fig. 14. Strong temperature fluctuation is due to plasma "pulsing": sound emission is enormous (similar to a chainsaw), thus in future sound recording will also be tested as additional tool to characterize this type of LAMPP. The plasma is rotated over the sample surface by the laser, as shown in Fig. 15. If the laser rotational frequency becomes too high, the plasma ball detaches from the surface of the sample and attaches in the process chamber at the site with the highest microwave field density, usually close to the microwave coupling window or antenna. Possibly because of the radial structure, no cracks are observed in the ceramic layer after cooling, as visible from Fig. 15.

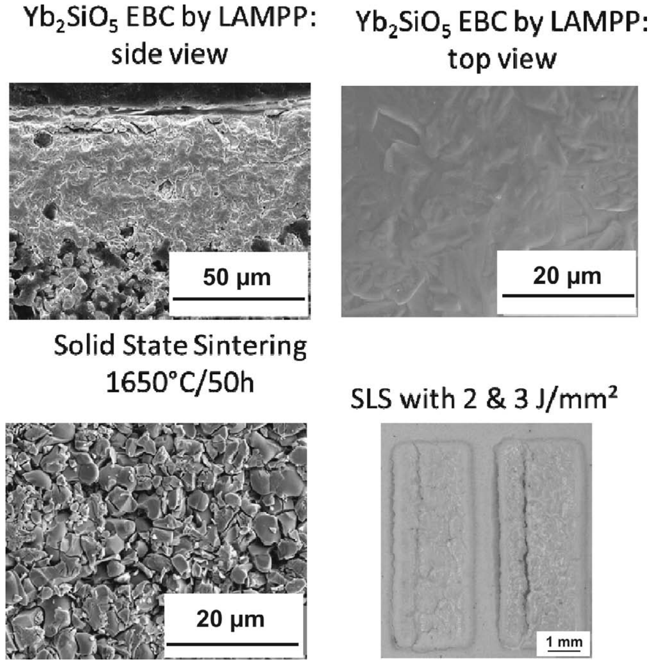

Fig. 13: SEM images of: top row LAMPP (graphite furnace, CO_2-laser) sintered ceramic coating obtained from Yb_2SiO_5 slip-cast on top of a Si_3N_4-$YbSi_2O_5$ porous ceramic (T_m Yb_2SiO_5 1950 °C) as compared to solid-state-sintered (bottom left) and selective-laser-sintered (SLS, bottom right) Yb-silicate ceramic powder.

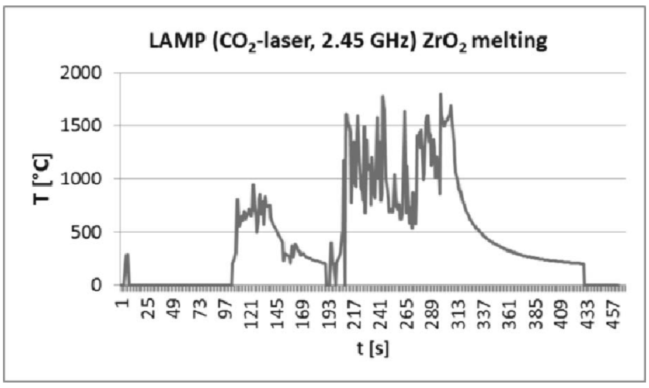

Fig. 14: LAMPP processing of ZrO_2-ceramics with pulsed CO_2 laser and < 1000 W microwave, cylindrical monomode cavity, ambient pressure, air. Heating profile recorded with a pyrometer, jumps in temperature are explained in the experimental section.

IV. Discussion

The concept of laser-confined microwave plasma as a processing tool for ceramic coatings derived from powders or by melting and solidification of an already dense ceramic has been experimentally investigated with the help of "in-house" built equipment. Although quite complex parameter sets had to be tested, finally a basic understanding of the major parameters influencing the ignition, sustainment and confinement of the plasma to a laser beam could be identified. The physical properties of the materials play a very important role with regard to the plasma ignition step. Similar to sintering, a "minimum temperature" is required to start the mass transfer either for sintering or for melting.

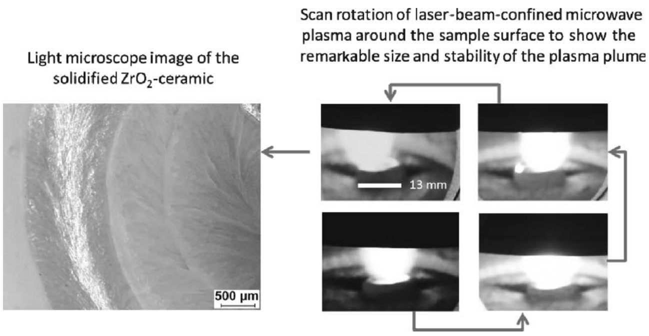

Fig. 15: LAMPP processing of ZrO_2-ceramics with pulsed CO_2 laser and < 1000 W microwave, cylindrical monomode cavity, ambient pressure, air. Light microscope image of the re-melted surface (left part of figure) processed by means of scan-rotation of the laser-beam-confined large and stable microwave plasma plume at the sample surface.

But, in contrast to sintering, this minimum temperature is not simply a fraction of the melting temperature: usually activation energy for sintering is in the order of 0.6 $T_{melting}$, (Taman Temperature), instead it depends on the type of species emitted from the surface upon heating and on the microwave absorption properties of the materials. For oxides, two groups of materials were identified: MIB-susceptible oxides that evaporate as molecular oxides followed by dissociation into metal atoms and oxygen, and oxides with electron emitter characteristics, which do not evaporate into metal atoms but are prone to electron emission in presence of a microwave field at elevated temperature. Such oxides can be subjected to LIB-based LAMPP. Confinement of the plasma with the help of the laser beam is crucial to overcome specific limitation of microwave energy absorption in solids and melts. Without laser confinement of the microwave plasma, process control and larger area surface treatment would not be possible because of limited penetration of the microwave field into a conductive hot ceramic piece or into a ceramic melt. Owing to the possibility of influencing the electron density of plasma in a wide range, with, for example, external pressure, type of gas, absorption upon heat dissipation (thermalization) in the sample or in the surroundings, recombination and scavenging, very efficient heating of a plasma plume with microwave radiation is possible. Plasma energy increase is not achieved with an increase in laser power, which would cause ablation, but by means of microwave absorption, which is transformed into heat and non-thermal electrons.

Our future work will concentrate on specific diagnostic methods that are required to characterize this new type of plasma processing of materials and improve process control.

V. Conclusions

LAMPP is a versatile new tool for processing ceramic materials. In particular, coatings derived from ceramic powders or by re-melting of a dense ceramic material can be obtained. A basic explanation of the ignition and the sustainment of LAMPP has been presented. The crucial role of the high-temperature physical properties of the materials subjected to LAMPP has been highlighted. With suitable parameters, sintering and melting of ceramics on top of different substrates is possible with low residual thermal stress and with almost no ablation, enabling the fabrication of crack-free coatings. The equipment developed so far for LAMPP needs further improvement of process control methods in order to become feasible for scale-up of this new coating technique.

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