Laser beam sintering of coatings and structures

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Abstract

Several novel techniques of ceramics sintering by laser beam have been tested successfully. Compact bodies as well as coatings of alumina were treated with CO_2- and Nd: YAG- laser beam. AlN was processed with an argon ion laser. The general difference between these procedures and conventional furnace sintering are the fastness and selectivity of the laser methods.

The results are presented together with a consideration of the advantages, limitations and possible applications. They verify the principle applicability of lasers for the sintering of ceramics and reveal insight into the mechanisms of the process.

1   Introduction

The research group "ceramics processing" at Laserinstitut Mittelsachsen e.V. focuses its investigative activities on the applicability of lasers for the processing of ceramics. After the successful development of a laser beam welding technique for ceramics the question arose, to which extent the thermal effect of a laser beam was suited for the

sintering of ceramic green bodies. Because of the laser's localized area of influence this method is qualified for the generation of a sintered body with a limited size. Thus the experiments confine to shapes with small dimensions.

From assays with compact pressed alumina green bodies a fundamental overview was gained on the influences of the process parameters upon the hardness of the resulting ceramic bodies.

The findings were applied to the generation of ceramic coating layers on metal surfaces. A technology was developed for the laser-sintering of powder layers of pure alumina. The layers were deposited onto steel substrates by an electrophoretic procedure, developed at the Fraunhofer IKTS Dresden as part of a joint research project. Applications can be anticipated as selective wear protection of metal surfaces. For this reason in the following experiments the hardness of the product is considered its figure of merit.

Future efforts aim at the generation of non-oxide ceramic layers or shaped modules with geometries in the range of micrometers by selective laser sintering. A sinter chamber, especially developed for non-oxide ceramics and the first results achieved with this device will be presented.

The presently available results verify the suitability of laser radiation for the sintering of oxide ceramics, though confined to modules or layers with sub-millimeter dimensions. Desired properties can be realised through the proper adjustment and control of the parameters during the process. The acquired qualities compare to the ones achieved by conventional sintering. Advantages of the laser sintering process are the considerably shorter process times, the option of selectivity, and the possibility to process a material or a composite under non–equilibrium conditions.

2 Materials and methods

2.1 Experimental set up for the oxide ceramics

Two lasers were applied: a continuous-wave (cw) operated Nd:YAG-laser and a cw-operated CO_2-laser. Due to the difference of the ceramic's absorption coefficients at the wavelengths of the mentioned lasers, each of the lasers affects the material specifically. The 1064nm wavelength of the Nd:YAG-laser is transmitted to a large extent and – in case of ceramic layers on a metal substrate – is back reflected from the metal into the ceramic layer by a high degree, thus heating the volume of ceramic material below the irradiated site almost evenly. The fibre-guided Nd:YAG beam was used defocused for the sintering of several square centimetres of ceramic coating. The CO_2- laser beam was also kept in a defined fixed position out of focus. Its wavelength (10,6µm), however, is absorbed almost completely in a depth which in technical terms is still attributed to the surface of the specimen. The motion of the CO_2-laser beam is accomplished with a scanner (Figure 1). Simultaneous measurement with a radiation pyrometer allows control of the ceramic surface temperature by tuning the laser power. Given temperature curves can thus be realised within an accuracy of +/- 10 K. The pyrometer is set for an experimentally determined 0.75 emission of the ceramic material.
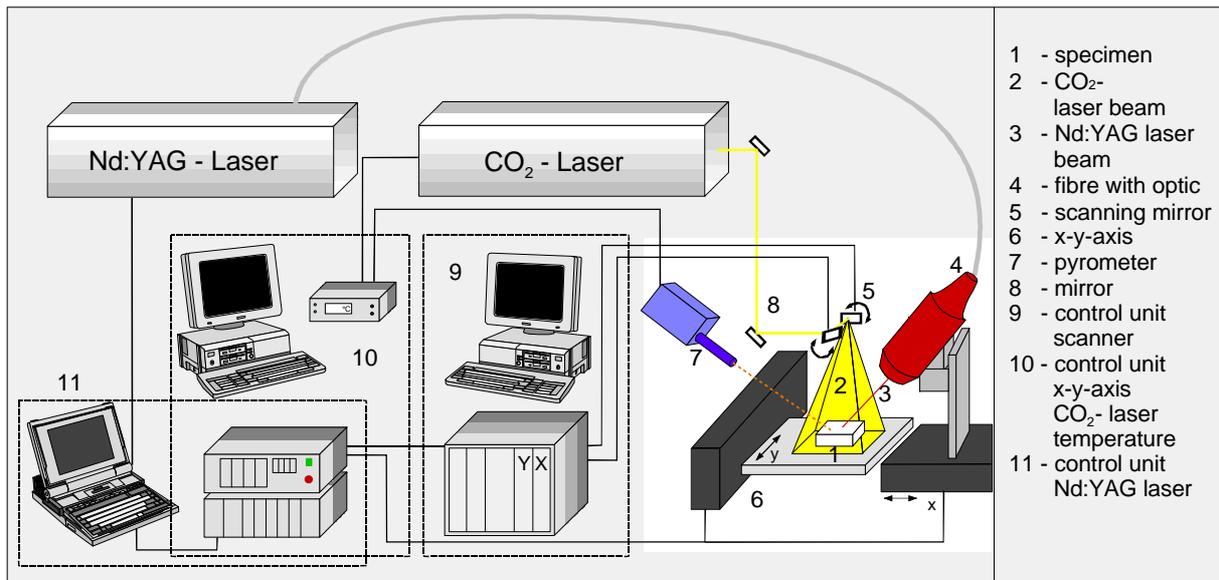
Figure 1

Experimental set-up

2.2   Sintering of compact green bodies

Assays were carried out with uniaxially cold-pressed (200MPa) α-Al_2O_3 specimens with a thickness of 2.5 mm and a mean grain size of 200 nm. A CO_2- laser beam was scanned over the surface; sinter temperature and its holding time were varied independently. Heating and cooling rates were maintained at a constant 5 Ks^{-1}.

2.3   Sintering of ceramic coatings

For the investigation of the sintering of ceramic coating layers steel (1.3981) sub-strates were coated electrophoretically with 5-10nm layer of α-Al_2O_3 powder with a grain size of 200nm[*]. The properties of the two materials are listed in Table 1. Be-cause of the reactivity of the steel at the sinter temperature the process was con-

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[*] The preparation of the specimens and the development of the ceramic layers were accomplished in cooperation with A. Krell, Fraunhofer IKTS Dresden.

ducted under Helium in a shielding gas chamber. The sintering was performed with both, the CO_2- laser and the Nd:YAG- laser.

Table 1

Composition of materials and their properties

	steel 1.3981		alumina
chemical analysis	Ni:	29 %	Al_2O_3 99.99%
	Co:	18 %	powder grain size: 200 nm
	C:	0.03 %	
	Mn:	0.3 %	
	Si:	0.2 %	
	Fe:	Residue	
Vickers hardness		150	2000 (as compact sintered body)
melt. temp.		1,450 °C	sintering temperature: 1100 °C
thermal expansion coefficient		7.6×10^{-6} K^{-1}	7.5×10^{-6} K^{-1}

2.4 Sintering of non-oxide ceramics

For the non-oxide ceramics sintering micrometer sized aluminium nitride powder blended with 1% yttrium oxide was cast into thin layers; after evaporation of the binder the thickness of the brown layers measured 30 µm. Selected partitions of the brown layers were scanned with the focused beam of the argon ion laser green lines. The probe was kept inside a chamber under an atmosphere of 4 bar Nitrogen or Argon to avoid dissociation or sublimation of the aluminium nitride. The function of the yttrium oxide is to combine with the alumina originating from impurities and from adsorbed oxygen to form a liquid phase.

2.5   Hardness measurement

Hardness measurements of the compact specimen were performed by the method of Vickers with a HMV 2000 (Shimadzu) according to the standard DIN 50 133.

Micro-hardness measurements of the sintered coatings were carried out with a method of dynamic loading, at a load of 20 mN, a loading rate of 0.44 mN s^{-1} within a period of 30 s at the centre of polished cross sections. These measurements were done by the Fraunhofer IKTS Dresden

3   Results

3.1   Laser beam sintering of compact ceramic bodies

The hardness of the laser-sintered compact bodies is displayed as a function of the sinter temperature and the holding time in Figure 2.
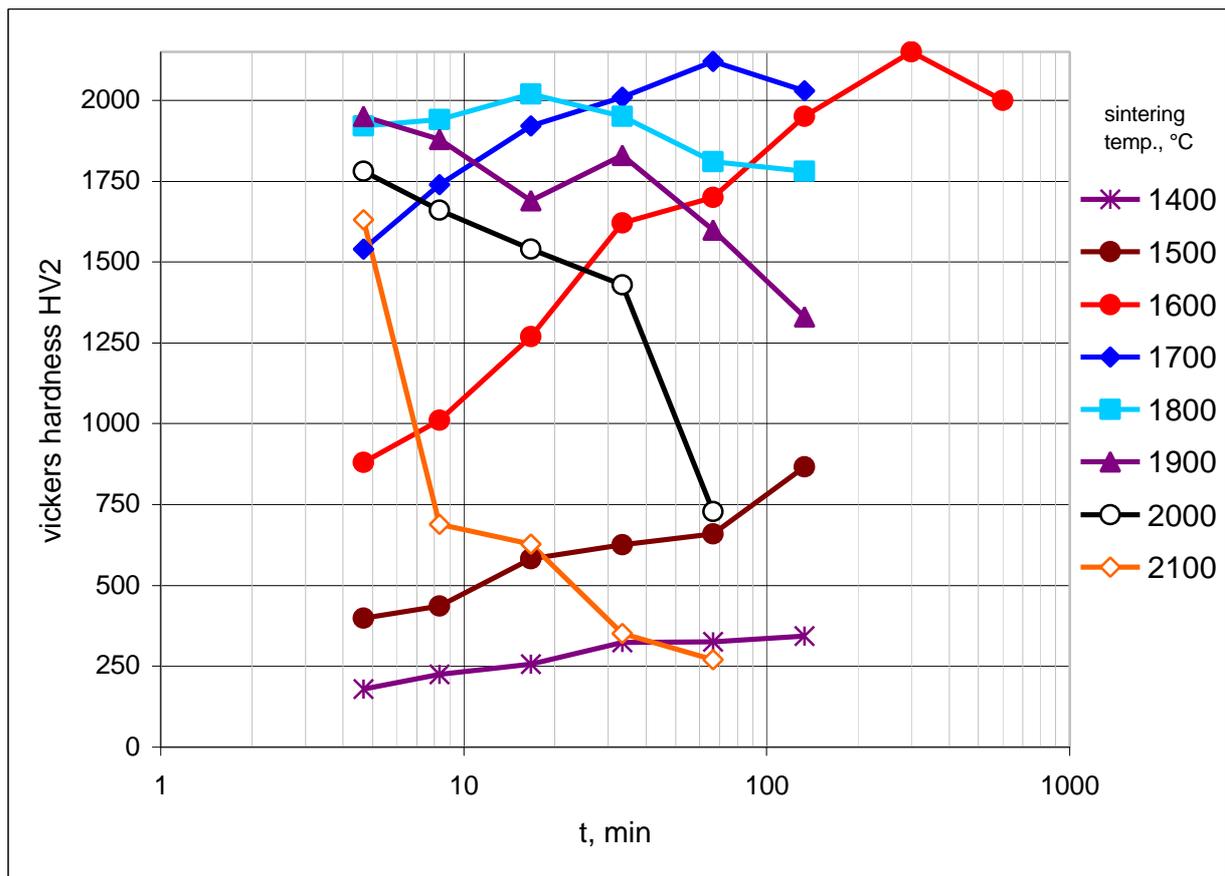
Figure 2

Dependence of the Vickers hardness on the sinter parameters

The results reflect the following mechanisms of material or structural conversion during sintering: First the heat induced in the green material initiates the formation of ceramic bonds between the crystals and the concomitant shrinking and compaction of the probe. As a consequence the hardness of the body increases. At further increase of temperature or a prolonged holding of the sinter temperature, after complete compaction, grain growth takes place preferentially. Lower degrees of hardness result under these conditions.

The highest hardness was obtained with a holding period of 300 min at 1600 °. Irradiation with a laser over such a long time is uneconomical. At higher sinter tempera-

tures there is - after a shorter holding time - another relative maximum of the hardness. It is , however, considerably lower than the achieved highest hardness. All the probes showed a 100% α-Al_2O_3 phase in XRD, independent of the process parameters.

Due to the high absorption of the laser radiation (60% of the energy is absorbed down to a depth of 1µm) a temperature gradient perpendicular to the surface is maintained during the sintering phase. The degree of compaction decreases consequently in the interior of the material below the surface (Figure 3).
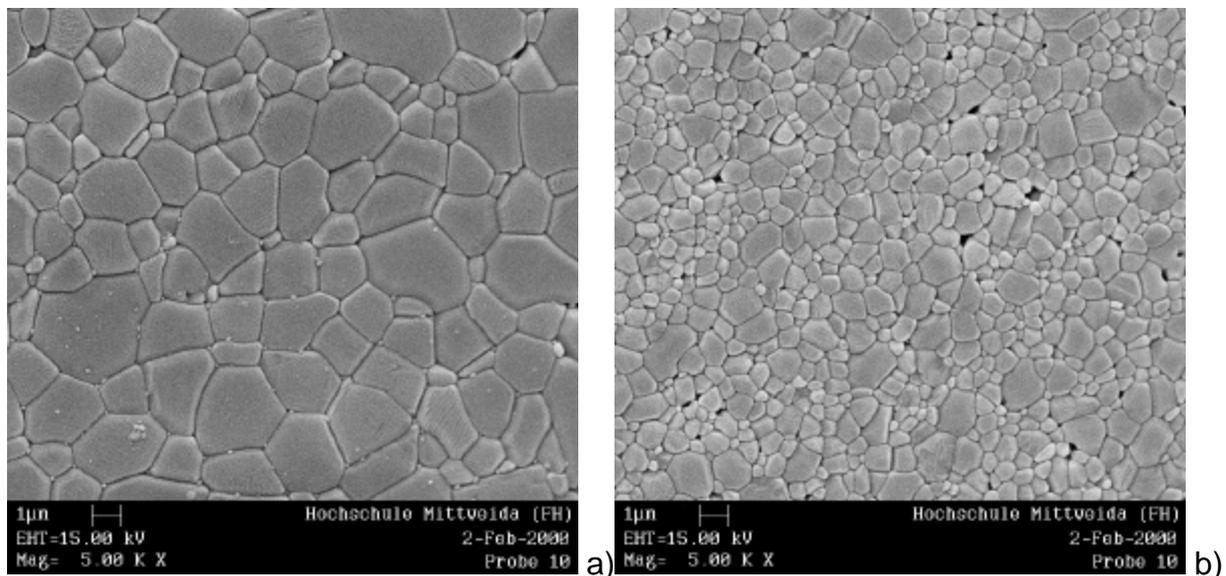
 a) b)

Figure 3

REM views of cross sections

    a) zone adjacent to the laser exposed surface

    b) zone adjacent to the surface on the remote side

Sinter temperature: 1900 °C

Holding time: 500 s

This effect is enhanced when the sinter temperature is raised together with a reduction of the holding time. The inhomogeneity of the compaction and sintering causes

uneven shrinking which results in tensional stress and deformation. The degree of shrinking becomes constant at a sinter temperature of 1800°C applied over a holding time of 1000s and attains a maximum of 20%.

Figure 4 shows the effect oft the sintering temperature upon the resulting grain size.
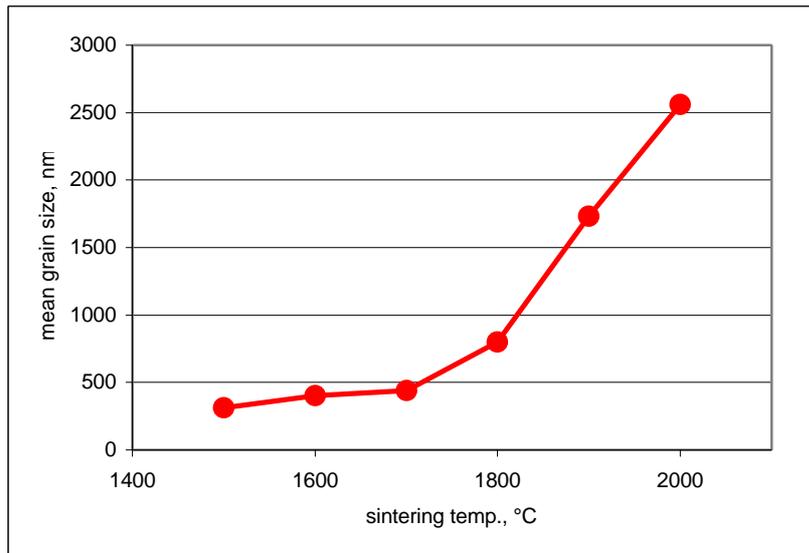

Figure 4

Dependence of the grain size on the sintering temperature (holding time= 500s)

3.2 Laser beam sintering of ceramic layers on metal

Under the mentioned conditions It proved impossible to generate ceramic coatings without cracks or fissures with the CO_2- laser. Sintering of the green layers could be accomplished; a pattern of fissures that spread across the coating, however, was observed attended by the flaking off of the sintered coating along the fissures.

By use of a Nd:YAG- laser crack-free and dense coatings became feasible. A small window of parameters could be found which produced the best results. Sintering temperatures just below the melting point of the metal permitted the generation of the intended properties of the coating within a minimum of time - about 400 seconds of

sintering time. Higher temperatures or a longer holding times resulted in bulk melting of the metal substrate. Lower temperatures required a longer holding time:

At a temperature of ϑ_s= 1,350 °C, about 700 s of sintering time are necessary; and at a temperature of ϑ_s= 1300 °C, the time needed for sintering increases to more than 2000 s.

The resulting coatings are characterised by:

- a very fine-grained structure

- high density

- high adherence

- no cracks at constant thickness of the layer.

A predetermined grain size can be produced by the proper choice of the parameters. The minimum grain size that leads to a densely sintered coating was found to be 250 nm (The original grain size was 200 nm). Porosity was less than 6 %. Figure 5b shows the cross section of the transition zone between coating and metal. A slight density gradient can be detected rising from the ceramic-metal interface towards the laser exposed surface. The resulting hardness, up to 20 GPa, is confirmed by two different laboratories. This means that the hardness of the coatings almost equals that of compact α-alumina.

20μm | EHT=15.00 kV | Mag= 500 X   200nn | EHT=15.00 kV | Mag= 30.00 K X   a)   200nn | EHT=15.00 kV | Mag= 30.00 K X   Hochschule Mittweida (FH) | 28-Mar-2001 | MT12-19 b)
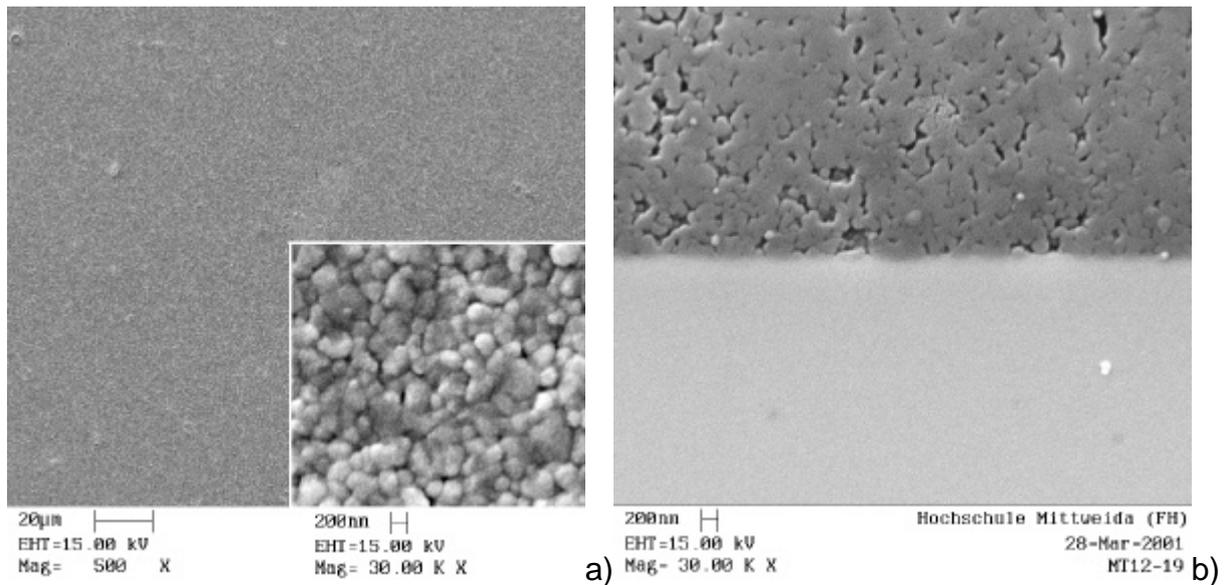
Figure 5

SEM view of:

a) the sintered coating surface with various magnifications,

b) the cross section

(thickness of the unsintered coating: 10 μm)

3.3 Laser beam sintering of non-oxide ceramics

Sintering of the above described brown material of AlN (1%Y_2O_3) resulted in a composite consisting of AlN crystals embedded in a solidified liquid phase. The liquid phase consists mainly of Al_2O_3 and Y_2O_3. As can be observed from Figure 6 and Figure 7, no crystal growth took place during the process.
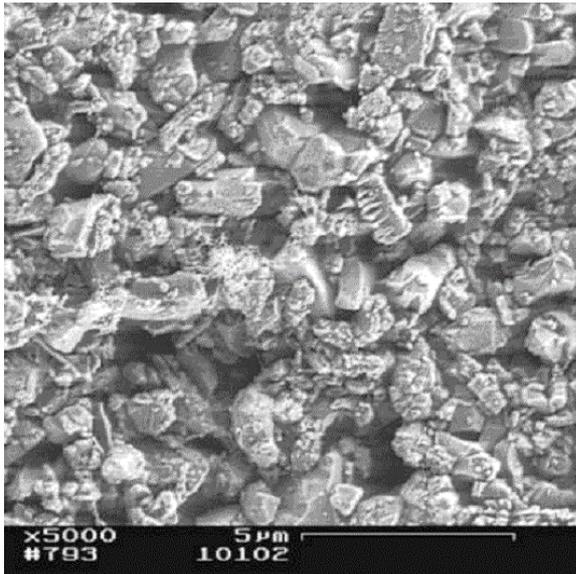
Figure 6

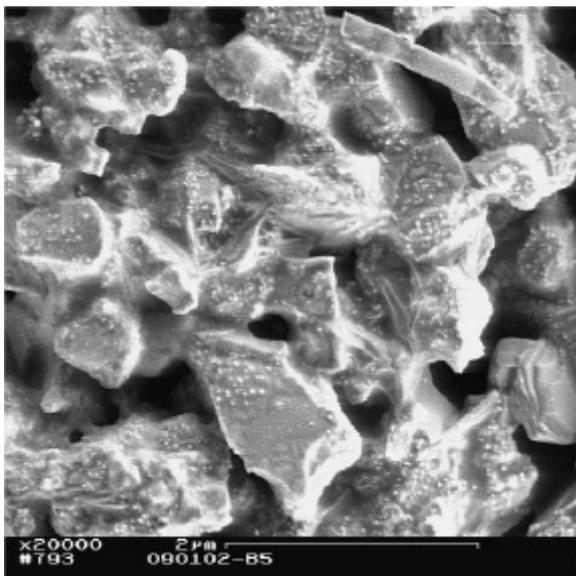SEM- view of the AIN brown layer

Figure 7

SEM- view of the AIN after sintering

4 Conclusions

Comprising the essence of the results, it has been shown, that laser beam sintering

of ceramics is feasible (special conditions have to be chosen for non-oxide ceramics).

The localized input of energy into the surface, however, causes heat gradients in the interior of the material which result in property gradients, which limit the range of applications. On the other hand this effect makes it possible to restrict the depth of the tool to defined zones at the surface of a body or at the interface of two components. Therefore its application will probably be confined to the generation or joining of ceramic layers, coatings or small ceramic bodies.