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Excimer laser induced melting and decomposition of technical ceramic surfaces and their properties

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ABSTRACT

The chemical, structural and topographical changes after the irradiation of technical oxide (Al_2O_3 , ZrO_2) and nonoxide ceramics (SiC , Si_3N_4) with a XeCl-Excimer Laser were studied as function of the applied energy density and number of pulses. The silicon-based nonoxide ceramics decomposed during a temperature and pressure induced process and an adherent up to 1,5 μm thick crystalline Si-layer remained on top of the specimen surface. In contrast, the oxide ceramics underwent a melting and rapid resolidification process without a chemical alteration. The minimization of surface defects on Al_2O_3 was used to generate a two-fold increase in Weibull's modulus m compared with untreated samples, whereas the silicon layer on top of SiC was helpful to generate and improve metal-ceramic joints between SiSiC and AlMgSi1.

1. INTRODUCTION AND OBJECTIVES

The treatment of materials with Excimer Lasers recently lead to some industrial realized applications, like the connection of sheet bares ^[1], the marking of surface mounted devices (SMD) and glasses ^[2] and the baring of wires ^[3]. With regard to the treatment of ceramics the recording of ablation rates and microstructuring was reposted. The aim of the present study is to exemplarily demonstrate the applicability of a one-step surface finishing technique for technical ceramics with an Excimer Laser, maintaining the fundamental dimensions of the workpiece. In addition, the chemical, structural and topographical changes after the irradiation should be determined and interpreted, respectively.

2. EXPERIMENTALS

2.1. Laser treatment

The surface treatment of the ceramics was carried out with a pulsed XeCl-Excimer Laser ⁽¹⁾ ($\lambda=308$ nm, pulse length 55 ns, maximum repetition rate 20 Hz). The gadget supplied a raw beam with an energy of 2 J, distributed over a rectangular raw beam geometry of 45 * 45 mm². The raw beam was focused onto the flat specimens using two 45° mirrors and an adjustable focus lense ($f = 300$ mm). The typical range for the parameters was 10 - 80 mJ/mm² for the energy density and 1 - 32 pulses per area. The variation in energy density was estimated to be smaller than 10%. The irradiation of the samples was obtained by a meander-like scanning ("flying" mode) of the flat specimens.

⁽¹⁾ Siemens XP 2020

2.2. Materials

The materials used in this study were commercial nonoxide ceramics, especially SiC and Si₃N₄ (SSiC, pressureless sintered SiC, SiSiC, silicon infiltrated SiC, HIPRBSN, hot isostatic pressed reaction bonded Si₃N₄) and oxide ceramics, like Al₂O₃ and ZrO₂ (Al₂O₃, 96%, 98% and 99,7% purity, Y-PSZ, Yttria partially stabilized zirconia, sintered and plasma sprayed), respectively. The combination of SiSiC and the aluminum alloy AlMgSi1 (3.2315) was selected for the diffusion welding of metal-ceramic joints.

2.3. Diffusion welding

The diffusion welding of AlMgSi1 versus SiSiC was carried out at 530° C/ 1h/ Air with an applied pressure of 25 - 31 N/mm². A sandwich construction of an aluminum sheet (40 * 40 mm², thickness 2 mm) between two SiC rings (outer diameter 35 mm, inner diameter 21 mm, thickness 7 mm) was used. Before joining the Al-sheet were cleaned in 10% HF, whereby the SiSiC underwent a Laser pretreatment.

2.4. Characterization

The topographical changes of the sample were monitored by roughness measurements according to DIN 4768 and DIN 4772 and expanded by Scanning Electron Microscopy (SEM) observation. The thickness of the modified surface layers was detected on fractured surfaces by the SEM technique. X-Ray Diffraction (XRD) and Auger Electron Spectroscopy (AES) revealed the chemical and structural changes after irradiation. The mechanical properties (hardness, Young's modulus) of the altered surfaces were monitored by microhardness tests (Load: 0,4 - 256 mN) using a Berkovich diamond indenter. The interaction of the components during diffusion welding was determined by Energy Dispersive X-Ray Spectroscopy (EDX) on polished cross sections. The shear strength τ of the joints was determined in comparison with glued samples (commercial two component epoxy glue) of the same geometry. Finally, the strength σ_{APB} of irradiated samples was determined by 4-point bending according to DIN 51110.

3. RESULTS AND DISCUSSION

3.1. Nonoxide Ceramics

As demonstrated for SSiC in Fig. 1, the surface roughness can be tailored in dependence of the applied energy density and the number of pulses. In general a roughening after the first pulse took place due to the cleaning of the surface. Medium numbers of pulses (4 - 8 pulses) lead to a minimized surface roughness. The surface consisted of a coherent resolidified layer. Surface defects like pores, which are visible in the untreated sample have been reduced. A further increase of the applied number of pulses generated a regular "hilly" structure, which is associated with an increase in roughness.

The irradiation of the silicon-based ceramics generated an up to 1 - 1,5 μm thick modified layer, Fig. 2 shows an example for SiSiC. XRD measurement, performed on SSiC, revealed the existence of crystalline Si-peaks.

Fig. 1: Roughness measurements of untreated and excimer laser treated SSiC

The comparatively large half-width of those peaks indicated a small crystallite size, caused by rapid solidification of the melted surface. Due to this silicon layer, the electrical conductivity increased by the factor 10^2 .

Fig. 2: SEM-pictures of untreated (left hand side) and excimer laser treated (30mJ/mm^2 , 8 pulses) cracked SiSiC-specimen

During the irradiation a temperature and pressure induced decomposition of SiC and Si_3N_4 took place, respectively. The pressure in the order of some kbar during the plasma development thermodynamically favoured the existence of a Si-rich melt, whereby C and N evaporated into the environment, respectively. AES measurements on SiSiC indicated a homogeneous distribution of Si and C up to a depth of about $1.5\text{ }\mu\text{m}$, whereby the Si-concentration increased approximately from 50 mole-% to 75 mole-% and as a countermove the C-concentration was reduced from 50 mole-% to 25 mole-%. For SSiC the Si-concentration was somewhat lower.

Application:

The Laser pretreatment of SiSiC enabled the formation of joints by diffusion welding with AlMgSi1. Without the pretreatment of SiC no joining took place. The joints withstood up to approximately $\tau = 58\text{ N/mm}^2$, whereas the glued samples only reached about $25 - 30\text{ N/mm}^2$. The specimens always fractured in the ceramic piece and typically shear lips with a 45° angle were observed. The EDX profile exhibited an interdiffusion zone of Si and Al of about $7\text{ }\mu\text{m}$ thickness.

3.2. Oxide Ceramics

Similar to the nonoxide ceramics the roughness of the oxide ceramics can be changed by the Laser treatment. For Al_2O_3 medium energy densities ($20\text{--}30\text{ mJ/mm}^2$) minimized the roughness, whereas large numbers of applied pulses (16-32) and higher energy densities (40 mJ/mm^2) roughend the surface.

A drastic surface smoothing can be achieved especially in the case of the plasma sprayed ZrO_2 . Reasons are the evaporation of tops and the fact that the lifetime of the melt exceeded the pulse duration (caused by the low thermal conductivity of zirconia), so that the melt flattens out on the top.

In contrast to the nonoxide ceramics no decomposition of the oxide melts took place and the surface layer underwent a melting and resolidification process. The surface of zirconia consisted of an up to $2\text{ }\mu\text{m}$ thick layer and an epitaxial resolidification took place. Cracks were always present and divided the surface into equally sized segments. These cracks were generated by tensile stresses during cooling. The surface of Al_2O_3 consisted of an $0.5 - 1\text{ }\mu\text{m}$ thick layer. An elimination of surface defects and pores was observed in those remelted layers.

The microhardness measurement (Fig. 3 a and b) performed on Al_2O_3 revealed three effects: (i) under the same load the indenter penetrates deeper into the Laser treated material (ii) with increasing indenter

displacement the load displacement curves and the slopes approached each other, respectively (iii) the hardness versus displacement curves and the SEM observations were in good agreement with hardness measurements of amorphous Al_2O_3 ^[4], which supported the assumption that the Excimer Laser treatment generated an amorphous Al_2O_3 top layer. Consequently, Young's Modulus was reduced to approximately 200 GPa compared with 400 GPa for the untreated material.

The reduction and elimination of surface defects on the alumina surfaces resulted in an increase in reliability. As an example, Weibull's Modulus m underwent a two-fold increase from $m = 7,8$ for the untreated material to $m = 16$ for the irradiated Al_2O_3 (30 mJ/mm^2 , 16 pulses) of 96% purity. With respect to the standard deviation, these effects are independent of the alumina purity^[5].

4. LITERATURE

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Fig. 3 a: Load-indenter displacement of untreated and excimer laser treated (30 mJ/mm^2 , 16 pulses) Al_2O_3

Fig. 3 b: Hardness of untreated and excimer treated (30 mJ/mm^2 , 16 pulses) Al_2O_3