Laser-Assisted Surface Modification of Alumina and Its Tribological Behavior

Feasibility for Application in Unlubricated High Performance Friction Systems

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High performance friction systems, e.g., dry clutches and brakes, require a good wear resistance and a friction coefficient that is nearly independent from sliding velocity and environmental conditions. Organic-based friction materials have reached their limitations regarding higher power densities. Engineering ceramics such as alumina (Al_2O_3) or silicon carbide (SiC) offer a great potential since remarkably higher thermal and mechanical loading is possible. However, the tribological performance of these monolithic ceramics is still insufficient. The aim of the present study was to assess the potential of a laser-assisted surface modification process in order to improve the tribological performance with regard to the application in dry friction systems. Therefore, commercially available alumina was modified using a newly developed laser-assisted preheating process and subsequent melting of the ceramic's surface using a CO_2 -laser and modification by additives such as TiC, TiN, B_4C , WC, ZrB_2 , Cr, Ni, Cu, and Ti. A systematic variation of additives and process parameters led to different multiphase microstructures. Subsequently, these were characterized using scanning electron microscopy and surface analysis methods (wavelength dispersive X-ray spectroscopy, energy dispersive X-ray spectroscopy). Finally, the tribological properties were investigated using a laboratory tribometer. The surface-modified ceramics were tested in unidirectional sliding motion against steel disks. The tribological results of the surface-modified ceramics were compared to those of monolithic Al_2O_3 and SiC ceramics and showed a reduced dependence of friction coefficient on sliding velocity. Moreover, the multi-phase ceramics possessed a higher wear resistance than the monolithic ones.

Keywords alumina, ceramics, ceramic matrix composites, dry sliding, laser-assisted surface modification, steel, tribology, wear resistance

1. Introduction

Basically, tribological systems can be divided into friction and sliding systems where requirements regarding friction are diametral.

Dry clutches or brakes representing unlubricated high performance friction systems, require a good wear resistance and a sufficiently high friction coefficient that is nearly independent from sliding velocity and environmental conditions. Currently, used organic-based friction materials have

reached their limitations regarding higher thermal and mechanical loads (Ref 1-4). A significant improvement of power density (i.e., a higher transferable torque at same design size for clutch systems) can not be achieved by using organic-based friction materials. Engineering ceramics such as alumina (Al_2O_3) and silicon carbide (SiC) offer a great potential since their inherent properties allow higher thermal and mechanical loads. However, considering comfort aspects important for consumer products such as automobiles, the tribological performance of these monolithic ceramics paired with steel disks is still insufficient and cannot compete with organic-based friction materials (Ref 5, 6).

Ceramics can be toughened by metallic particles or interdependent metallic networks as shown for alumina with nickel (Ref 7-9) and nickel aluminide (Ref 10). Due to their compatibility and properties also alumina with addition of nickel, silver, molybdenum, copper, iron, chromium, and chromium-nickel has been investigated (Ref 11). Chromium is of special interest since its thermal expansion is lower than the one of alumina. Consequently, fracture toughness of alumina could be increased by addition of chromium particles (Ref 12).

In order to improve the tribological properties an alteration/modification of one surface in contact is sufficient (Ref 13-15). There are several different methods which can be used for a surface modification of alumina such as physical vapor deposition (PVD), chemical vapor deposition (CVD), etc.

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Another possibility is the laser-assisted surface modification that has already shown its potential in the past. For alumina a CO₂-laser (wavelength 10.60 μm) is well-suited since nearly 100% of the laser output power can be used for machining or treatment (Ref 16, 17). One advantage of laser-assisted surface modification is the decrease in grain size by remelting which results in improved mechanical properties. For alumina-based refractories a laser-assisted surface treatment with CO₂ or diode laser led to columnar grain and reduced the open porosity (Ref 18). By applying a dual beam process combining a CO₂ and diode laser a modified zone of about 2.5 mm in depth with a pore-free and almost crack-free microstructure could be achieved (Ref 19). Moreover, surface melting of monolithic ceramic and simultaneous addition of selected powders produces a ceramic composite. Depending on the melting point of the used powders these modification methods are either called laser-alloying or laser-dispersion. A laser-alloying of an alumina-based refractory was achieved by CO₂-laser-assisted surface melting combined with flame-spraying of an Al₂O₃-Cr₂O₃ powder mixture (Ref 20). Higher feed rates led to a finer microstructure and thermally induced cracking was reduced by statistically supported selection of the process parameters. Further studies showed that by using precoating and injection processes as well as a suitable selection of powder additives in CO₂-laser-assisted surface modification it was also possible to improve the tribological performance in lubricated (Ref 21, 22) and in unlubricated systems (Ref 13, 23-28) as well as under cavitation loading (Ref 29, 30).

The motivation for the present study was to improve the tribological performance of monolithic alumina as well as to improve the applied laser-assisted processing. Consequently, the produced composite materials were thoroughly analyzed and tested in unidirectional dry sliding to assess their feasibility regarding their application in dry friction systems.

2. Materials and Experimental Methods

2.1 Reference Materials

Reference materials were the commercial Al₂O₃ ceramic F99.7 produced by Friatec and the sintered SiC (SSiC) ceramic EKasicF produced by ESK Ceramics. The ceramics were used as cylindrical pins ($D = 16$ mm, $h = 7$ mm) with spherical end faces ($R = 100$ mm). The counterbody for tribological testing was a disk ($D = 60$ mm, $h = 8$ mm) of the normalized steel C45E (DIN EN 10083) with a Vickers hardness of 206 ± 6 HV30. This steel was chosen in order to have a well-defined quality steel which is able to deform plastically in normalized condition under the applied tribological loading and consequently offering a good wear resistance. Moreover, it can be subject to further heat treatment if needed.

The microstructures of the different materials are shown in Fig. 1. Selected properties of all materials used in this investigation are summarized in Table 1. The alumina (F99.7) had an average grain size of 7.5 μm (Fig. 1b). The SiC

Table 1 Selected properties of reference materials used in this investigation

	Grain size, μm	Hardness HV	Thermal cond. (a), W/(m K)
SiC (EKasicF)	1.9	2540	110
Al ₂ O ₃ (F99.7)	7.5	1670	30
C45E	30.0	206	45

(a) Determined at 25 °C

Fig. 1 SEM micrographs of the materials used in this investigation: (a) alumina Al24, (b) alumina F99.7, (c) EKasicF (SiC), and (d) steel C45E

(EKasicF) had a significantly lower average grain size of 1.9 μm (Fig. 1c). The microstructure of the plain carbon steel C45E in normalized condition was ferritic-pearlitic with an average grain size of ca. 30 μm (Fig. 1d). The pearlitic fraction was about 40%. It was determined visually by means of SEM imaging and subsequent image analysis methods.

2.2 Laser-Assisted Surface Modification Process

The substrate material used for the laser-assisted surface modification was the alumina Al24 (Friatec) with an open porosity of ≤ 5 vol.% and an average grain size of 30 μm (Fig. 1a). The geometry of the pins was the same as for the reference ceramics.

The added powders were titanium nitride (TiN), titanium carbide (TiC), tungsten carbide (WC), boron carbide (B_4C), zirconium boride (ZrB_2), and a commercially available mixture of chromium (Cr) and nickel (Ni) with a volume ratio of 1:4 as well as pure nickel (Ni), titanium (Ti), and copper (Cu). SEM micrographs of the powders can be found in Fig. 2(a)–(j). The ratios of the different powder mixtures as well as the average particle size of the different powders for the surface-modified ceramics Al24-TTB, Al24-WT, Al24-ZbCN, and Al24-WTNCT are given in Table 2. Particle sizes were determined visually by means of SEM imaging and subsequent image analysis methods. The chosen powder compositions were based on the results of previous experiments and on analytical considerations regarding the reduction of thermally induced stresses in the ceramic matrix composite material.

2.2.1 Preheating. A laser-assisted preheating process was newly developed in order to avoid cracking due to thermal shock loading during surface modification. A schematic is shown in Fig. 3. A laser-scanner system (with F-Theta planar lens made of ZnSe, $f = 250$ mm) was mounted under 45° to the vertical beamline. In order to achieve a scanning contour without geometrical distortion, i.e., a perpendicular radiation on the surface, a parallel orientation of specimen surface and laser-scanner system was necessary. Therefore, a pneumatically actuated table was designed. The specimen's surface temperature was logged continuously during the preheating process using a pyrometer (type IGA 140, manufacturer Impac) with a measuring range of 350–2500 $^\circ\text{C}$. Using this facility it was possible to heat the specimen's surface. Scanning velocity was 10.5 m/s and laser power was increased continuously from ca. 50 W (minimum power of the used laser source) up to a maximum of 700 W. Different scanning contours were investigated (cf. Fig. 3a, b). The meander contour (a) was selected as standard geometry since the parabolic spiral (b) showed some overheating in the central area of the pin that was probably caused by improper scan path accuracy.

One disadvantage of using a CO_2 -laser is the small penetration depth of the radiation. In order to reduce thermally induced stresses due to temperature gradient between the specimen's top and bottom during preheating the process was further improved by additionally using an infrared-radiator at the bottom of the ceramic pin (cf. Fig. 4).

2.2.2 Surface Modification. Basically, two methods were used for laser surface modification: a single- and double-stage process. For both processes the newly developed laser-assisted preheating process as described above was used (cf. Fig. 3).

At the single-stage process (Fig. 5a) powder mixtures were injected directly into the laser-induced molten pool of the ceramic pin after preheating of its surface to 1400 $^\circ\text{C}$. The

CO_2 -laser used for surface modification (type SMP400P, FeHa) had a maximum power of 480 W. The laser mode was TEM₀₀ leading to a Gaussian beam intensity distribution. The laser beam size diameter was 12 mm and a point focus optics with $f = 250$ mm at a working distance of 220 mm was used. The resulting laser spot size was approx. 1.5 mm. The used coaxial powder nozzle (type Coax9, Fraunhofer IWS-Dresden) allowed a direction-independent modification of the alumina surface. The contours of the laser for the different modifications are shown in Fig. 6. The feed rate during the single-stage modification was 250 mm/min, cf. Table 2. The spirals were designed in such a way that the molten pool of the ceramic was overlapping by about 20%. Starting point was the inner region of the pin since thermal shocking is smaller in this case. The start time of the injection process was automatized using a computerized numerical control (CNC). Because of the lower melting points the metallic powders were injected in a second process step using lower laser power (cf. Fig. 6c). The main advantage of the single-stage process is reducing the thermal load of the powders. Thus, also powders with lower oxidation resistance can be used. One disadvantage was that the particle size of the additives should not be smaller than about 5 μm due to conveying limitations.

At the double-stage process (Fig. 5b) the ceramic substrate (Al24) was precoated using a sedimentation process. For this a suspension of powders and an organic solvent (2-propanol) was prepared and applied on the surface. In order to reduce oxidation processes during heating an additional layer of alumina powder was applied on top using the same process. The precoated substrate was preheated to 1200 $^\circ\text{C}$ with additional argon-flushing. For melting the surface and consequent dispersion or alloying with the added powders the scan velocity was decreased to 790 mm/min and simultaneously the laser power was adjusted to 200 W, cf. Table 2. The advantages of this process are smaller thermal shock loading due to immediate modification after preheating and the possibility to use powders with a particle size significantly smaller than 5 μm .

The process parameters for the surface-modified ceramics Al24-TTB, Al24-WT, Al24-ZbCN, and Al24-WTNCT are presented in Table 2.

2.3 Tribological Investigations

Tribological investigations were performed in air at a relative humidity of 50% at unidirectional, unlubricated sliding motion using a pin-on-disk tribometer (Plint, TE92HS). Ceramic pins made of SiC (EKasicF) and alumina (F99.7) as well as the surface-modified ceramics were tested against C45E steel disks. The ceramic pins were fine ground on the spherical side ($R = 100$ mm) to an area of 8 mm in diameter by using a diamond disk (D25). The steel disks were fine ground using a corundum grinding wheel (EK200). A schematic view of the tribological test setup is given in Fig. 7. The normal load of 100 N applied during the tests resulted in a nominal contact pressure of 2 MPa. Five velocity ramp cycles (ramp time $t_r = 6$ s, holding time $t_h = 8$ s, and $v_{\text{max}} = 12.6$ m/s) were performed at different starting temperatures of the disk (55 $^\circ\text{C}$, 70 $^\circ\text{C}$, 85 $^\circ\text{C}$). Velocity profiles shown in Fig. 7 are idealized. In order to ensure that running-in processes were finished, a whole block, consisting of 15 ramp cycles, was repeated. Only the second one was used for further data analysis. The average sliding distance for one test comprising

Fig. 2 SEM micrographs of the powders used for laser-assisted surface modification of alumina: (a) TiC, (b) TiN fine, (c) B₄C, (d) TiN coarse, (e) WC, (f) ZrB₂, (g) Cr + Ni (1:4), (h) Ni, (i) Cu, and (j) Ti

Table 2 Source materials (powder mixtures) as well as process parameters for the surface-modified ceramics Al24-TTB, Al24-WT, Al24-ZbCN, and Al24-WTNCT

	Al24-TTB	Al24-WT	Al24-ZbCN	Al24-WTNCT
Powder ratio, vol.%(particle size, μm)	33 TiN (1.7) 33 TiC (2.0) 33 B ₄ C (9.0)	50 WC (5.1) 50 TiN (7.5)	50 ZrB ₂ (3.8) 50 Cr + Ni (1:4) (16.3)	33 WC (5.1) 33 TiN (7.5) 17 Ni (4.7) 8 Cu (62.4) 8 Ti (51.6)
Process	Double-stage	Single-stage	Single-stage	Single-stage
Preheating temperature, °C	1200	1400	1400	1400
Feed rate, mm/min	790	250	250	250
Contour	Fig. 6(a)	Fig. 6(b)	Fig. 6(c)	Fig. 6(b)
Laser power P_{L1} , W (a)	200	100	120	80
Laser power P_{L2} , W (b)	...	...	60	...
Line energy S_1 , J/mm	15.2	24	28.8	19.2
Line energy S_2 , J/mm	...	...	14.4	...
Theoretical powdervol. $\dot{V}_{P1}$, mm ³ /s	...	0.125	0.125	0.125
Theoretical powdervol. $\dot{V}_{P2}$, mm ³ /s	...	...	0.076	...
Conveyor pressure, bar	...	2.5	1.5	1.5
Argon flow rate $\dot{V}_{Ar}$, l/h	Flushing	60	60	60

The average particle sizes are given in brackets
(a) First injection
(b) Second injection

Fig. 3 Schematic of laser-assisted preheating process including investigated scan contours

Fig. 4 Schematic of specimen fixture with additional IR-radiator for laser-assisted preheating and surface modification. Al25 is alumina with an open porosity between 20 and 30% produced by Friatec

30 ramp cycles was 5760 m. Normal load, friction moment, disk temperature at the circumference (start criterion), and temperature within the wear track were recorded continuously

during the tests. Before and after testing the specimens were examined by optical 3D-profilometry (confocal white light profilometer, Fries Research Technology) and linear wear of the steel disk was determined at eight lines. Linear and volumetric wear of the pins was determined by measuring the diameters of the pin's contact surface at four positions prior to and after tribological testing and applying the known geometric relations. Reported values are the average of at least two identical tests.

3. Results and Discussion

3.1 Surface Modification

3.1.1 Microstructure. Figure 8 shows BSE images of the surface-modified ceramics. The Al24-WT was produced by a single-stage process (i.e., by injecting titanium nitride and tungsten carbide) and is depicted in Fig. 8(a). The powder additives are still in their initial particle form and partly melted at the interface. Due to differences in their atomic numbers tungsten carbide appears white and titanium nitride light gray in the BSE image. Figure 8(b) shows the microstructure of Al24-TTB that was produced by a double-stage process, e.g., precoating with titanium nitride, titanium carbide, and boron carbide. No particles are found. There is a reaction phase at the grain boundaries instead, appearing gray in the BSE image. Grain size is between 5 and 10 μm . The Al24-ZbCN that was produced by a single-stage process is shown in Fig. 8(c). It was produced by injecting of zirconium boride as well as a mixture of chromium and nickel (volume ratio 1:4). No particles are found. Besides metallic conglomerates there is a reaction phase at the grain boundaries as for the Al24-TTB, appearing white in the image. Grain size is with values between 2 and 5 μm significantly smaller than for the Al24-TTB. The interfacial bond appears to be weaker with increasing size of the metallic conglomerates that are up to 200 μm in size. In Fig. 8(d) the

Fig. 5 Schematic of laser-assisted surface modification process: (a) single-stage and (b) double-stage process

Fig. 6 Contours for the laser-assisted surface modification: (a) concentric circles for double-stage process, (b) in-out spiral for single-stage process, and (c) in-out-reverse spiral for injection of metal powders

Fig. 7 Schematic of the tribological test setup and parameters as well as the geometry of the ceramic pins

modified ceramic Al24-WTNCT is shown. This ceramic was produced by injection of tungsten carbide, titanium nitride, nickel, copper, and titanium, i.e., by a single-stage process. Metallic conglomerates with WC and TiN particles are found. The interface between conglomerates and matrix material is good. Moreover, there is a reaction phase in the alumina matrix.

Powder additives with high melting point are well distributed in all surface-modified ceramics. This can be explained by mixture in the ceramic molten pool by the so-called Marangoni flow that is described for instance in Ref 31. The depth of the surface modification for all presented variants is approx. 0.5 mm and is shown exemplarily for Al24-WT in Fig. 12(a).

3.1.2 Chemical Analysis. The surface-modified ceramics were chemically analyzed using EDX or WDX, respectively. Results are shown in Fig. 9. The determined volume fractions are listed in Table 3.

WDX-analysis of Al24-WT (Fig. 9a) shows TiN and WC particles nearly in their initial shape. However, they are partly melted at the interface. WC particles possess a titanium-rich edge. Matrix material is Al_2O_3 . For the Al24-TTB (Fig. 9b) the resulting reaction phase is titanium-rich. No boron could be detected. It was possibly oxidized and evaporated during the modification process which has been already observed in Ref 32 for sintering processes. Matrix material is Al_2O_3 . The Al24-ZbCN (Fig. 9c) shows in EDX-analysis a zirconia-rich reaction phase at the grain boundaries. Metallic conglomerates in the alumina-matrix consist of a mixture of the elements chromium and nickel. A small percentage of nickel and a significant share of chromium are dissolved in the alumina matrix or are present in the reaction phase at the grain boundary. By means of EDX-analysis no boron was detected. As for the Al24-TTB most likely the boron compound was oxidized and evaporated during the modification process. Analysis of the Al24-WTNCT by EDX-element-mapping (Fig. 9d) shows that the matrix consists of Al_2O_3 . Within the matrix there is a titanium-rich reaction phase at the grain boundaries. Moreover metallic conglomerates are inside the matrix. These consist mainly of nickel, titanium, and a small proportion copper. Inside the conglomerates WC and TiN particles can be found.

Fig. 8 SEM micrographs (BSE images) of the surface-modified Al_2O_3 -ceramics: (a) Al24-WT, (b) Al24-TTB, (c) Al24-ZbCN, and (d) Al24-WTNCT

Table 3 Resulting microstructural constituents and hardness of surface-modified specimens Al24-TTB, Al24-WT, Al24-ZbCN, Al24-WTNCT and substrate ceramic Al24 (Al_2O_3)

	Al24	TTB	WT	ZbCN	WTNCT
Microstructural constituents, vol.%	Al_2O_3	RP 17 ± 7 Al_2O_3 balance	WC 15 ± 4 TiN 7 ± 2 Al_2O_3 balance	RP 17 ± 3 CrNi 7 ± 7 Al_2O_3 balance	RP 10 ± 6 TiN 12 ± 7 WC-Ni-Cu-Ti 20 ± 8 Al_2O_3 balance
Closed porosity, %	≤ 5	≤ 3	≤ 1	≤ 3	≤ 2
Vickers Hardness, HV0.1	1153 ± 429	1928 ± 212	1988 ± 259	2061 ± 354	1150 ± 472

RP: reaction phase

3.1.3 Mechanical and Thermophysical Properties. Mechanical as well as thermophysical properties of the surface-modified layers were determined. Hardness of surface-modified ceramics as well as the substrate material Al24 was measured at microsections perpendicular to the specimen's surface at minimum 10 positions. Hardness of the substrate material (ca. 1200 HV 0.1) could be improved by suitable laser-assisted surface modification almost by a factor of two (ca. 2000 HV 0.1). One exception is the Al24-WTNCT where only the hardness of the substrate material is reached. Due to great differences in the initial hardness of the injected powder additives, i.e., WC, TiN, and the metallic components Ni, Cu, and Ti, values of overall hardness possess a great scatter.

The effective thermal conductivity of the compound of modified layer and substrate material was determined as a function of temperature. Therefore, specimens of 1 mm thickness were prepared that consisted of 0.5 mm modified layer and 0.5 mm substrate layer. The thermal diffusivity and heat capacity were measured applying the laserflash method and differential scanning calorimetry respectively. Subsequently, these values

were used to calculate the effective thermal conductivity λ_{eff} . Figure 10 shows the determined effective thermal conductivities of the different specimens. Surface-modified ceramics as well as substrate ceramic show a decrease in thermal conductivity with increasing temperature as one would expect. The Al24-TTB and Al24-WT have significant higher values than the substrate material Al24. However, the Al24-ZbCN shows a lower thermal conductivity. This can be explained by chemical reaction from ZrB_2 to ZrO_2 during the modification process while the boron evaporated. Zirconia has a thermal conductivity that is one order of magnitude lower than for alumina. The highest values in effective thermal conductivity shows Al24-WT with 55 W/(m K) at room temperature. The Al24-TTB has a value of 32 W/(m K), the Al24-WTNCT 28 W/(m K) and finally the Al24-ZbCN showing the lowest value with 15 W/(m K). However, at a temperature of ca. 800 °C there are only little differences between the different materials.

3.1.4 Thermally Induced Cracking. After preheating and modification process a radial crack was visible, cf. Fig. 11, at the bottom side of the ceramic pin. Depending on

Fig. 9 Chemical analysis of surface-modified ceramic pins: (a) Al24-WT, WDX-Mapping of elements Al, W, and Ti; (b) Al24-TTB, WDX-Mapping of elements Al, O, and Ti; (c) Al24-ZbCN, EDX-Mapping of elements Al, Zr, Ni, and Cr; (d) Al24-WTNCT, EDX-Mapping of elements Al, Ti, W, Ni, and Cu

Fig. 10 Effective thermal conductivity λ_{eff} of surface-modified ceramic pins and of substrate ceramic Al24 (Al_2O_3) as reference

Fig. 11 Ceramic pin after surface modification: (a) pin bottom side, a radial crack is visible and (b) pin upper side with modified surface area, edge cracks are visible adjacent to the modified surface area. Cracks were emphasized by application of the dye penetration method

the used powder composition the pin also had edge cracks at the pin upper side adjacent to the modified surface area. The Al24-WT had also a crack network in the modified surface area, cf. Fig. 12.

These cracks can be attributed to different types of thermally induced stress. During preheating there is a temperature gradient within the ceramic pin mainly between upper and bottom side resulting in the observed radial crack. At the laser surface modification there are thermally induced stresses after re-solidification due to thermal mismatch (different coefficients of thermal expansion) as well as the different Young's moduli of ceramic composite at the modified area and unaltered pin material. This might have led to the observed edge cracks. The reason for the crack network within the Al24-WT could be mainly attributed to the great differences in thermal expansion and Young's moduli of tungsten carbide (WC) and alumina. For the Al24-WTNCT the plasticity of the metallic phases might have reduced the thermally induced stresses leading to an almost crack free surface-modified area.

Please note that none of the above-mentioned cracks were affecting the mechanical integrity of the pin during tribological testing, i.e., no failure of the pin occurred.

3.2 Friction and Wear Behavior

3.2.1 Friction. In Fig. 13 the coefficient of friction as well as the track temperature on the metallic disk is shown over sliding velocity for the different surface-modified ceramics. The displayed curves are averaged for starting temperature 70 °C. Couple F99.7/C45E (gray curves) is included as reference. Up- and downward ramps are indicated by corresponding arrows. All couples show a decreasing coefficient of friction with increasing sliding velocity in upward and downward ramps. Reasons for decreasing coefficient of friction with increasing sliding velocity are still topic of current research work and have not yet been fully understood. Suggested possibilities are adhesional effects which are more pronounced at lower sliding velocities and thermal effects, i.e., higher temperature at the interface leads to lower coefficient of friction for higher sliding velocities.

For Al24-WT/C45E the value of the coefficient of friction decreases from 0.55 at 1 m/s after a short increase to 0.61 to a value of 0.32 in the upward ramp and from 0.50 at 1 m/s to 0.23 at 12 m/s in the downward ramp (Fig. 13a). In comparison to F99.7/C45E the decrease of the coefficient of friction is not as pronounced and friction level is slightly higher. The track temperatures (Fig. 13b) during the upward ramp increased from

Fig. 12 Surface modification Al24-WT: (a) cross section, modification depth is approx. 0.5 mm, some cracks perpendicular to the surface are visible and (b) top section, a crack network is visible

Fig. 13 Tribological behavior of surface-modified ceramic pins mated against the steel C45E (black curves): coefficient of friction and track temperature T_1 , respectively, vs. sliding velocity. (a, b) Al24-WT, (c, d) Al24-TTB, (e, f) Al24-ZbCN, and (g, h) Al24-WTNCT. Averaged curves at a starting temperature of 70 °C are depicted. Arrows indicate up- and downward ramps. Gray curves show reference couple F99.7/C45E

68 °C ($v = 1$ m/s) to a value of 90 °C ($v = 12$ m/s). This curve trace is almost congruent with the reference. During downward ramp the track temperature remains constant at values of 120–130 °C. This is a significantly higher niveau than the reference.

Couple Al24-TTB/C45E is shown in Fig. 13(c) and (d). The coefficient of friction decreases from 0.60 to 0.31 in the upward

ramp and from 0.55 to 0.23 in the downward ramp. Curves are similar to the reference. However, they show a slightly smaller decrease of the coefficient of friction. The track temperatures in the upward ramp decreases from 62 °C ($v = 1$ m/s) to a value of 90 °C ($v = 12$ m/s) and are partly 10 K below reference couple F99.7/C45E. In the downward ramp track temperature

remains relatively constant at values of 110 °C and are thus almost congruent with the reference.

Figure 13(e) and (f) depicts the frictional behavior of couple Al24-ZbCN/C45E. Coefficient of friction decreases from 0.76 to 0.35 in the downward ramp. In the upward ramp a decrease from 0.70 to 0.30 is observed. In comparison to the reference friction niveau is significantly increased for up- and downward ramps. In the upward ramp track temperature increases from 71 to 105 °C. The final temperature is significantly higher than the temperature of the reference. During the downward ramp the track temperature shows only small variations with values between 125 and 130 °C. The track temperatures during the downward ramp are between 20 and 25 K higher than the ones of the reference couple F99.7/C45E.

The behavior of the surface-modified pin Al24 -WTNCT is displayed in Fig. 13(g) and (h). The coefficient of friction has more temporarily variations than all other couples. In the upward ramp the values decrease at a sliding velocity range from 1 to 12 m/s from 0.75 to 0.33 and in the downward ramp from 0.76 to 0.25 and thus higher than the reference. However, this couple shows a more pronounced dependence on sliding velocity than the reference. The track temperature increases from 68 to 108 °C. For higher sliding velocities the temperatures are significantly higher than the ones of the reference F99.7/C45E. During the downward ramp the track temperature is about 125 °C which is between 15 and 20 K higher than the reference.

Friction behavior was quite stable after a certain running-in period of the first whole block for all tested couples. A stable third body layer has developed during this block consisting of 15 ramp cycles. In order to verify this for extended tribological loading additional long-term tests for F99.7, EKasicF, and Al24 -ZbCN mated with C45E were carried out. These tests showed that frictional behavior is also stable for longer sliding distances or periods, respectively, i.e., friction stability for these materials seems to be sufficient.

3.2.2 Wear. The volumetric wear coefficient k_v of all investigated couples is shown in Fig. 14(a). All couples show similar disk wear of about $6.5 \times 10^{-6} \text{ mm}^3/(\text{Nm})$ except the couples with Al24-WT and EKasicF with k_v values of 7.8×10^{-6} and $8.8 \times 10^{-6} \text{ mm}^3/(\text{Nm})$, respectively. Lowest pin wear shows the Al24-TTB couple with $1.1 \times 10^{-7} \text{ mm}^3/(\text{Nm})$. Al24-WTNCT and Al24-ZbCN are close with values of $1.9 \times 10^{-7} \text{ mm}^3/(\text{Nm})$. F99.7 couple is slightly lower with $1.5 \times 10^{-7} \text{ mm}^3/(\text{Nm})$. Al24-WT shows with a value of $2.9 \times 10^{-7} \text{ mm}^3/(\text{Nm})$ highest pin wear

of all investigated surface-modified ceramics. Highest overall pin wear has the EKasicF with an amount of $4.9 \times 10^{-7} \text{ mm}^3/(\text{Nm})$. A possible reason could be a thinner, mainly metallic third body layer resulting in stresses nearer at the ceramic surface that led to granular fractures of the SiC as observed in SEM imaging. Another reason are possible oxidation processes ($\text{SiC} + \text{O}_2 \rightarrow \text{SiO}_x + \text{C}$) due to high contact temperature during tribological loading.

Linear cumulative wear, i.e., summing up the amounts of pin and disk, is shown in Fig. 14(b). Couple Al24-TTB/C45E has the lowest value with 4.7 μm . After this follow the couples with Al24-WTNCT and Al24-ZbCN showing values of 5.7 or 6.0 μm , respectively. Highest cumulative wear of all couples with surface-modified pins shows couple Al24WT/C45E with a value of 8.9 μm . Reference couple F99.7/C45E shows a linear cumulative wear of 5 μm while EKasicF/C45E has an amount of 11 μm . A reason for the low cumulative wear of the Al24-TTB couple could possibly be the microstructure with an interdependent reaction phase at the grain boundaries leading to less susceptibility to granular fractures of the ceramic and therefore also less abrasion for the steel disk, since there are less abrasive acting ceramic particles in contact. The addition of metallic particles might also be beneficial due to similar reasons. However, this is mainly caused by the metallic conglomerates, cf. Al24-WTNCT and Al24-ZbCN.

3.2.3 Material Selection. Specific system properties are necessary for using the investigated couples in unlubricated high performance friction applications. Demands on dry clutch systems regarding their design and therefore also to some extent their materials are defined after (Ref 33) as follows:

- temperature independent coefficient of friction
- positive friction gradient $d\mu/dv$
- temperature resistance
- high coefficient of friction $\mu \geq 0.4$
- good adaptation of contact couples
- optimized heat removal (e.g., heat transfer over flywheel or pressure plate)
- very good clutch control
- high lifetime due to low cumulative wear
- insusceptible to multiple media (e.g. oils, greases)
- low overall weight
- high power density for reducing design space
- tolerant failure behavior
- rotational speed resilience

Fig. 14 Wear behavior of the investigated couples: (a) volumetric wear coefficient of the pin $k_v(\text{pin})$ vs. $k_v(\text{disc})$ and (b) linear cumulative wear of pin and disk

Characteristic values relevant for application in dry clutches and investigated within the scope of this study are depicted in a spider chart in Fig. 15. Shown values are for downward ramp of selected couples in order to facilitate a material selection. The characteristic values are: the volumetric wear coefficient k_v of the disk as indicator for lifetime, the minimal coefficient of friction $\mu_{12.5 \text{ m/s}}$ as measure for friction niveau, the friction gradient $d\mu/dv$ as measure for comfort behavior and finally the quasi-static coefficient of friction $\mu_{0.001 \text{ m/s}}$ as indicator for torque transmission. The different criteria and target values are based on desired system properties as well as experiences with conventional organic-based friction materials and were defined as follows: k_v (disk) of $5 \times 10^{-6} \text{ mm}^3/(\text{Nm})$, $\mu_{12.5 \text{ m/s}}$ of 0.40

Fig. 15 Spider chart of selected tribological indicators for selected surface-modified and monolithic ceramics mated against the steel C45E for standard conditions (cf. Fig. 7), downward ramp

Fig. 16 Average friction gradient $d\mu/dv$ of downward ramp vs. the effective thermal conductivity $\lambda_{200 \text{ °C}}$ of selected surface-modified ceramics at 200 °C mated against the steel C45E

as well as the average friction gradient $d\mu/dv$ with a value greater than $-0.005 \text{ (m/s)}^{-1}$ and a quasi-static coefficient of friction $\mu_{0.001 \text{ m/s}}$ of 0.40. An important issue regarding comfort is the friction gradient that should be close to zero or even positive in order to avoid excitation of the drive train.

All depicted couples fulfill the target value for the quasi-static coefficient of friction $\mu_{0.001 \text{ m/s}}$. The highest value of 0.51 shows by far couple Al24-ZbCN/C45E. Certainly, the target value minimal coefficient of friction $\mu_{12.5 \text{ m/s}}$ as measure for friction niveau can not be fulfilled by any shown couple, but the couples with Al24-ZbCN and EKasicF are the most promising. The target value for disk wear, k_v (disk) of $5 \times 10^{-6} \text{ mm}^3/(\text{Nm})$, is based on experiences with organic/cast iron couples and due to higher abrasion ratio for ceramics quite ambitious. Nevertheless, it is only slightly missed by some of the investigated couples. These are especially the couple with Al24-TTB, showing the smallest disk wear, followed by couples with F99.7 and Al24-ZbCN. The potential for improvement by laser-assisted surface modification compared to the reference F99.7/C45E can be clearly seen for couples with Al24-WT/C45E as well as Al24-TTB/C45E. However, the target value for comfort behavior ($d\mu/dv$) is not reached by any of the couples. EKasicF/C45E shows a slightly better behavior than Al24-WT/C45E.

Another interesting issue regarding differences between surface-modified and monolithic ceramics is discussed below. In Fig. 16 the average friction gradient $d\mu/dv$ for the downward ramp is plotted over thermal conductivity of monolithic ceramics aluminium nitride (AlN), EKasicF (SiC), and F99.7 (Al_2O_3) or effective thermal conductivity of surface-modified pins at 200 °C. The aluminium nitride was tribologically investigated under the same conditions. Please note that the determined thermal conductivity of AlN is lower than literature values, however, it corresponds to the material quality used in this investigation. The average friction gradient increases with temperature. Moreover, regression lines of surface-modified ceramics and monolithic ceramics possess different slopes. Remarkably, lower effective thermal conductivities of surface-modified pins already lead to similar friction gradients as for the monolithic ceramics.

4. Conclusions

It can be concluded that a higher power density and therefore a decrease in required design space for dry clutch systems can be achieved due to the higher thermal and mechanical load-bearing capability of ceramic/steel couples compared to conventional organic-based friction materials mated with cast iron. A suitable laser-assisted surface modification of alumina can improve the tribological behavior, especially pin and disk wear as well as friction niveau and quasi-static friction. Some efforts have still to be made to achieve a better performance of these materials in high performance friction systems especially regarding the friction gradient. In order to exploit the given advantages and to reduce the major disadvantage—still possessing an insufficient friction gradient—an electro-mechanical control system could be possibly applied in unlubricated high performance friction systems, e.g., dry clutches, since frictional behavior seems to be quite stable after a certain running-in period, i.e., after a stable third body layer has developed, as observed during tribological tests.

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