Surface processing of zirconia ceramics by laser

Tero Kumpulainen*,[1], Arnold Ismailov[2], Leo Hyvärinen[2], Erkki Levänen[2] and Jorma Vihinen[1]

[1]Mechanical Engineering and Industrial Systems, Tampere University of Technology
[2]Materials Science, Tampere University of Technology
P.O.Box 589, FIN-33101 Tampere, Finland
*Corresponding author: tero.kumpulainen@tut.fi

Abstract

The aim of this study was to investigate phase transformations and glazing of zirconia bulk ceramic as a function of laser processing parameters. Zirconia-based ceramics have good material properties for a variety of applications. The main advantage of zirconia compared to other structural ceramics, like silicon-based ceramics and alumina, is its high fracture toughness (typically over 10MPa√m). This property is largely based on partial stabilization of zirconia, where a portion of the material is in metastable phase, enabling instantaneous phase transformation under mechanical load. This consumes energy otherwise provided to crack propagation. The stable phase of zirconia to exist in room temperature is monoclinic; therefore a rapid cycle of heating and cooling is necessary for achieving metastable tetragonal phase. Pulsed laser processing offers just the right type of thermal cycle for the aforementioned phase transformation to occur. In this study a nanosecond pulsed laser was used for surface processing of zirconia ceramic blocks.

During laser processing high energy can be concentrated into small area, causing sudden local heating, which in turn causes material to melt and vaporize instantly. However, heat dissipation remains small due to the short pulse length, leading to the desirable cycle. Temperatures in the process correlate with several parameters: pulse width, peak energy, repetition rate, pulse overlap, material properties and wavelength. Zirconia is a tough material to process in terms of material removal with laser ablation, since it tends to melt rather than evaporate.

1.0 Introduction

Zirconia based materials have characteristics that are beneficial for multiple applications, such as dental industry[1,2], coatings[3,4,5,6], oxygen sensors[7], high temperature fuel cells and artificial joints[8]. One processing method to make further modifications to the material is laser processing. An example of such an application in addition to the laser coating and sealing is the modifying of cell adhesion of a ceramic material. [9] Partially stabilized zirconia materials have high strength, high toughness, high hardness, and good wear properties. These properties have been most commonly achieved in multi-phased zirconias by adding yttria, ceria, magnesia or alumina to stabilize zirconia to a metastable phase in room temperature. The three main phases for zirconia are monoclinic, tetragonal and cubic. Monoclinic (m) and cubic (c) are stable phases, as tetragonal (t) is a metastable phase. One challenge with zirconia ceramics in general is the tetragonal to monoclinic transformation, which may occur if material concentration is not correct for the application and ambient environment. The allotropic phase transformation in zirconia is known to occur by a martensitic twinning mechanism with dependence on material composition, temperature, stress, and environment. Monoclinic and tetragonal have different characteristics and they affect wear and mechanical properties of the material. Laser processing is an attractive option for producing structured or modified surfaces on zirconia ceramics, since it does not reduce the phase transformation capacity of the material. On the contrary, it has been proven to reduce the amount of monoclinic phase in the material [2, 6], thus possibly even increasing the materials resistance to fracture.

Zirconia is a tough material to process in terms of material removal with laser ablation, since it tends to melt rather than evaporate. Consequently, it also has a tendency to form a glaze type surface when processed.[6] Bärsch et al.[10] studied the effect of using a liquid film for the ablation, and concluded that it is recommendable to cover ceramics in thin layer of liquid when laser processing. Using different type of laser from fs to ns pulse width enable different type processing, concerning machining quality and process speed. Femtosecond and picosecond ultrashort pulse lasers are generally considered to enable the finest and the most accurate features with good quality. However switching from ns to fs pulses does not always have desired improvement, as laser-induced incubative defect formation has effect both in ns and fs processes with YSZ.[11] Hence ns pulse width implemented process can provide good quality, but enable via shorten processing time better productivity. Laser re-melting and treatments of zirconia material is used for modifying coatings. Antoua et al.[12] studied using laser in situ and improving microstructure of the thermal spraying and Jasim K.M.[13] studied laser sealing of the thermal sprayed coatings. There have been made several studies, which use NIR wavelength laser to process zirconia based material. Many of them report that NIR wavelength is not the best alternative and processing in NIR is a thermal process which causes cracks.[2, 14] However Dear et. al. [14] say in the conclusion that by choosing correct parameters cracking may be avoided and NIR laser suits drilling and cutting zirconia well. In this study Mg-PSZ (magnesia-doped partially stabilized zirconia) was used for testing the effects of laser processing on potential phase transformations and glazing effects.

2.0 Experiment and materials

In this study laser processing was implemented with a nanosecond fibre laser at 515 nm wavelength. Pulse width of 17 ns was used for processing the ceramic pieces. Surface features were produced with a Scanlab Hurry scan II galvo scanner. The scanner was used to enable high beam speeds and accurate and flexible control of the beam.

The ceramic surfaces were engraved with grooves ranging from 0.8 to 3 µm in depth, while distance between two adjacent grooves was kept constant. Deep grooves and grooves processed with higher pulse energy were a bit wider than the low power made equivalents, hence line separation was adjusted to compensate the few micrometres change in the single groove width. Main cause for the groove width variation is the intensity distribution of the laser beam. Processing with Gaussian beam tends to form v-shaped grooves, which shape is dependent of the processing parameters. When several passes are used material surface behaves differently at each pass, as absorption changes according to the processing parameters. In the centre, where most of the peak energy is located, material melts and vaporizes instantly, whereas at the edges of the spot beam energy is reduced to the point where it is not high enough to ablate material. In this area material is heated and melted. Additionally, according to material characteristics, this material tends to rather melt than vaporize, which can be seen in the surface of the material after processing.

In addition to the pulse energy, the amount of passes was varied to get information about the effect of the pulse energy on the behavior of the processed pattern. Thus the number of passes had to be increased, when pulse energy was reduced. Usually low power enables better quality, especially if the end form cannot be achieved with single pass. This was true also for this case, visual appearance of the grooves made with low power was better, but as processing takes longer time total heat load was higher. However, peak temperature was assumed to be lower due to the pulse energy reduction.

All samples were processed with lines in one direction, as processing with lines in several directions would make the beam cross over parts of already processed material, affecting the results. Absorption of the beam is different on pure material than on the material that has surface already being modified. Making lines in both directions and studying its effect was left for future work.

Beam velocity and repetition rate was kept constant during the processing at 10 kHz and 100 mm/s accordingly except the one test set. In this test pulse overlap was increased by reducing beam velocity to get information about the greater heat input. Parameters are presented in table 1.

Beam velocity was chosen according to the repetition rate to keep pulse overlap small. Small overlap was chosen to minimize heat load. With the chosen parameter combination, the groove is continuous and individual pulse shape can be recognized, but pulse overlap is small enough for the process to be efficient. Higher pulse overlap often results in deeper groove with a single pass, but process becomes more sensitive to the processing parameter due to higher thermal load. Materials with good heat conduction can be seen wider heat affected zone, whereas poor heat conduction leads to high thermal gradients.

Samples were analysed with SEM. In addition to the cross-section and surface analyzing, an EDS and XRD analysis was performed. The content, phases and other potential changes in the material due to the processing were analyzed. Results were compared to polished and untreated reference samples without any laser processing.

All samples were ground and polished with identical steps: 220, 600 and 1200 grit grinding discs, after which 3- and 1-micron diamond paste was used for polishing. This was to ensure good surface quality, get rid of residual cracks and minimize the effect of the uneven and porous surface of bulk material. All flaws could not be removed, due to the inherent porosity of the material. The effects of these flaws were taken into account in the final analysis.

3.0 Results and discussion

The SEM images show cracking with every processing parameter, as it was expected, see **Virhe. Viitteen lähdettä ei löytynyt.** However, there are some noticeable differences between samples made with different pulse energies. In the **Virhe. Viitteen lähdettä ei löytynyt.** some of the cracks have been highlighted with red color to improve visibility.

In the sample 1 (**Virhe. Viitteen lähdettä ei löytynyt.**a), cracks are more random and do not have any specific orientation, as opposed to sample 4 (**Virhe. Viitteen lähdettä ei löytynyt.**d) where cracks form v-shaped pattern. It can be seen that cracks have initiated from the edges and proceed to the center pointing at the direction of the processing. One possible reason for this would be that there is a difference in cooling rate between the edge and centre part of the groove. The centre would be in a molten state for a longer period of time, resulting in a slight delay in fracturing. This would cause the cracks to follow the path of the processing beam, essentially pointing to the direction of the processing. In samples 3 and 2 (**Virhe. Viitteen lähdettä ei löytynyt.**c and **Virhe. Viitteen lähdettä ei löytynyt.**b respectively) the cracks have formed more in the perpendicular direction to the groove, but also randomly between horizontal cracks. In the case of sample 1 (**Virhe. Viitteen lähdettä ei löytynyt.**a) a single pass made with 40µJ produced a groove less than 1µm deep.

The crack area is the smallest in the bottom right figure 1d where cracks form a volcano shaped pattern. These crack lines are the longest and some of them extend from the edge to the middle to point where two crack lines meet. This groove was made with 45µJ pulses, which suggests the reason for the cracks that follow direction of the processing. On the other hand high pulse energy leads to the higher peak temperature, but increases the amount of heat conducted. Ceramics are often good insulators, and hence resist heat conduction, causing cracks, as temperature gradients within the material can be high.

Analyzing the sample surfaces with an optical microscope supports the SEM findings: the grooves made with low pulse energy are smoother than the ones produced with high power. In the **Virhe. Viitteen lähdettä ei löytynyt.**, higher magnification of the modified surfaces on samples 1-4 is presented.

The **Virhe. Viitteen lähdettä ei löytynyt.**d shows that the highest power made groove, cracks open up more, especially at the edges of the groove. The difference between samples is not high when comparing grooves made with S2 and S4 (shown in Figure 2b and 2d, respectively), but difference can be seen when comparing figures 2c and 2d, where lowest and highest pulse energy made grooves are shown. Grooves in the S3 are the smoothest of all samples. Amount of the recast in the unprocessed area between grooves is also lowest for this sample. Unprocessed area is almost clear of the small-size debris that can be seen in Figure 2a, 2b, 2d, and **Virhe. Viitteen lähdettä ei löytynyt.**.

Processing time wise making grooves with 15µJ takes double the time compared to the 45µJ made groove. On the other hand, total energy consumed was 1,5 times compared to the 15µJ made groove, which explains the thermal effects. Additionally, it should be noted that as the groove width and depth are bit larger with high power, the total amount of material removed is not the same for both. By combining the number of repetitions, pulse energy, and approximate amount of the material removed, the process energy efficiency can be evaluated. Efficiency of the 45µJ laser pulse energy is approximately the same or a bit higher than with the 15µJ pulse energy.

Smooth surface has its benefits, but for some cases rough surface can also be desirable. Rougher surface quality can be beneficial in some processes such as medical application, where nanostructures and/or small microstructures of few microns in size may enhance surface characteristics or when fast processing of large areas is required. Efficient processing combined with good performance would enable economical production and better product.

The topographic difference between previously discussed samples is more noticeable when inspected in lower magnification, see **Virhe. Viitteen lähdettä ei löytynyt.**. Burr shape is different and thickness seems to be smaller, as melting plays larger role when processing with higher power. With low power cracking occurs, but melting is controlled better compared to the processing made with high pulse energy. Most of the energy is used to ablate material, and the single pulse effected area is smaller both in depth and width. High pulse energy will melt large area at once, and amount of melted material is higher than with lower pulse energy. Ablated material has also effect to the process. Ablated material will affect the melt, and ejecting material transfer parts of the molten material to the edges, where it solidifies again. With low power, near threshold energy usually the process is optimal and most of the material is ejected directly from the groove minimizing burr and recast.

In the test where pulse overlap was increased, the effect was straightforward with the higher power made results. Increasing average power and increasing pulse overlap will both cause additional heating within the material. Hence increasing pulse overlap does not bring benefits that would emphasise using it during processing.

When a cross-section of the sample 3 was analysed, it became apparent that even the sample produced with the smallest pulse energy has melted material on the edge of groove. In this case the height of the melted material is about 1µm. With higher pulse energy made samples, height of the burr was almost same according to the SEM images, but difference was smaller than was estimated from the microscope images. Another difference between low and high pulse energy made features is the shape of burr, in the **Virhe. Viitteen lähdettä ei löytynyt.**shown shape is smoother than with the higher pulse energy. According to the microscope analyses it could be assumed that the finest features are cracked during sample preparation or are present in the area between grooves. From the **Virhe. Viitteen lähdettä ei löytynyt.**can be seen black spot that correspond to pores in the material.

3.1. EDS- and XRD-analyses

In the **Virhe. Viitteen lähdettä ei löytynyt.**, the composition of the sample material according to EDS is shown in mass percent (wt%). According to these results, laser processing has very minor or no effect on the molecular structure of the material. The deviations are so small that when taking uncertainty into account, effects and reliable analyses cannot be made.

Rietveld refinement was used for attempting to see indication of minute changes in phase ratios. XRD analysis from the sample 4 is shown in the **Virhe. Viitteen lähdettä ei löytynyt.**. Most of the monoclinic phase at the surface was removed during the polishing before laser processing, so laser processing seems to have little to no effect. However, results show that laser processing does not cause undesirable t->m change either, which is good for the material characteristics. Table 2 shows the phase ratios of key samples.

In this part of study was used two wavelengths to get more detailed information about the laser processing. According to the XRD results, increasing pulse energy with the 1030nm wavelength reduced monoclinic phase and converted it into cubic phase. Same applies to the 515nm made tests. However, changes between the samples 1-4 are small and the amount of cubic, tetragonal and monoclinic phases remain essentially same with all samples, when the uncertainty of the analysis is taken into account. With the highest power made in NIR wavelength sample additional monoclinic phase appeared to convert into tetragonal phase equalling the polished before processing state. According to the XRD analysis, main cause for the achieved tetragonal phase proportion, as laser processing increases mostly the cubic phase within the material. Turning tetragonal portions to cubic would somewhat hinder the t à m phase transformation capability of the zirconia, possibly resulting in smaller fracture toughness values. It seems, however, that in our case the amount of tetragonal phase is not severely decreased. There might be a slight increase in the amount of cubic phase, but most likely at the expense of monoclinic phase.

The combined effect of polishing and laser treatment was studied by processing two blocks with same laser parameters, see table 1, S8. First block was polished and second was at its untreated state. According to the XRD measurements the phases are almost identical with both samples. Result confirm that polishing has quite a small effect on the end result, as all the phases are almost identical. The reliability of the XRD in analysing the laser treated area and depth seems sufficient, since the method easily detected the outermost layer that had high concentration of monoclinic phase on an untreated surface. It is safe to assume, that the depth range of the XRD-analysis does not exceed that of the melted material or HAZ produced by laser.

4.0 Conclusion

The main results of this study confirm a lot of the findings reported by previous research on the field:

- Laser processing of Mg-PSZ produces a surface with no more monoclinic phase than before processing. In fact, the amount of monoclinic phase is found to significantly reduce when unpolished zirconia surfaces are treated. This means that with right parameters, laser can be used for the same function as high-temperature furnace treatment for reverting some t à m transformation occurring over time or due to air humidity.
- The phase transformation toughening capacity of Mg-PSZ was not hindered, since the amount of tetragonal phase remained roughly the same regardless of laser processing parameters used for producing grooves on the material surface.
- The glazing effect appeared within the whole range of parameters that were applied to laser processing of Mg-PSZ in this study. It was noted, however, that the pattern of cracking was not identical for all the parameter sets. Bringing a large amount of energy with a single sweep produced a cracking pattern that followed the direction of processing. This is apparently a result of cooling rate differences between various regions of the processed groove.

There still remains a lot to be investigated regarding the effect of laser processing parameters on zirconia ceramics, especially the types that incorporate multi-phase structure. One suggestion for future studies would be testing lower pulse energies, to the point where material is not evaporated or even melted. This would hypothetically enable observing phase transformation behavior without the distraction of the glazing effect.

References:

1. Delgado-Ruíz RA.; Calvo-Guirado JL.; Mate-Sánchez JE.; Ramirez-Fernández P.; Guardia J.; Gomez-Moreno G. "Zirconia dental Implants with Femtosecond Laser Microstructuring. A new way to guide cell growth" 19th Annual Scientific Meeting of the European Association of Osseointegration 6-9 October 2010, Glasgow
2. Noda M.; Okuda Y.; Tsuruki J.; Minesaki Y.; Takenouchi Y.; Ban S. "Surface damages of zirconia by Nd:YAG dental laser irradiation" Dental Materials Journal; 2010 Vol 29 no.5 p. 536

3. Tsai, H.L.; Tsai, P.C. "Laser glazing of plasma-sprayed zirconia coatings" Journal of Materials Engineering and Performance 1998 vol. 7 p. 258
4. Batista, C.; Portinha, A.; Ribeiro, R. M; Teixeira, V.; Costa, M. F.; Oliveira, C. R.; Surface laser-glazing of plasma-sprayed thermal barrier coatings. Applied Surface Science, 2005 vol. 247 no.1, p. 313.
5. Rabiee S.M.; Azizian M.; Nourouzi S. "Influence of zirconia on microstructure of bioactive glass coated on stainless steel for biomedical application" International Conference on Biomedical Engineering (ICoBE), 2012 27-28 February,Penang vol. no. p. 109
6. Lee J.-H.; Tsai P.-C.; and Chang C.-L. "Microstructure and thermal cyclic performance of laser-glazed plasma-sprayed ceria–yttria-stabilized zirconia thermal barrier coatings," Surf. Coatings Technol., 2008 vol. 202, no. 22–23, p. 5607
7. Radhakrishnan, J.K.; Kamble, S.S.; Krishnapur, P.P.; Padaki, V.C.; Gnanasekaran, T., "Zirconia Oxygen Sensor for aerospace applications," Sensing Technology (ICST), 2012 Sixth International Conference on ,2012 vol., no., p.714
8. Piconi C.; Burger W.; Richter HG; Cittadini A; Maccauro G.; Covacci V.; Bruzzese N.; Ricci GA.; Marmo E." Y-TZP ceramics for artificial joint replacements." Biomaterials. 1998 vol. 16 p.1489
9. Bärsch N.; Gatti A.; Barcikowski S. "Improving Laser Ablation of Zirconia by Liquid Films: Multiple Influence of Liquids on Surface Machining and Nanoparticle Generation" JLMN-Journal of Laser Micro/Nanoengineering 2009 Vol. 4, No. 1 p. 66,
10. Hao L.; Lawrence J.; Chian K. S. "Osteoblast cell adhesion on a laser modified zirconia based bioceramic" Journal of Materials science: Materials in Medicine 2005 vol. 16 p.719
11. Heiroth S.; Koch J.; Lippert T., Wokaun A.; Günther D.; Garrelie F.; and Guillermin M. "Laser ablation characteristics of yttria-doped zirconia in the nanosecond and femtosecond regimes " Journal of Applied Physics 2010 107, 014908
12. Antoua G.; Montavonb G.; Hlawkaa F.; Corneta A.; Coddetb C.; Machic F. "Modification of ceramic thermal spray deposit microstructures implementing in situ laser remelting" Surface and Coatings Technology 2003 vol. 172 p. 279
13. Jasim K.M. "Laser sealing of zirconia–yttria–alumina plasma sprayed coating" Journal of King Saud University – Engineering Sciences 2013 vol 25, p. 11
14. Dear F.C.; Shephard J.D.; Wang X.; Jones J D.C.; Hand D.P. " Pulsed Laser Micromachining of Yttria-Stabilized Zirconia Dental Ceramic for Manufacturing" Int. J. Appl. Ceram. Technol., 2008 vol. 5 no.2 p.188
15. Fernandez R.; Meschke F.; De Portu G.; Anglada M.; Llane L. "Fatigue and Fracture Characteristics of a Fine-grained (Mg,Y)±PSZ Zirconia Ceramic" Journal of the European Ceramic Society 19 1999 p. 1705

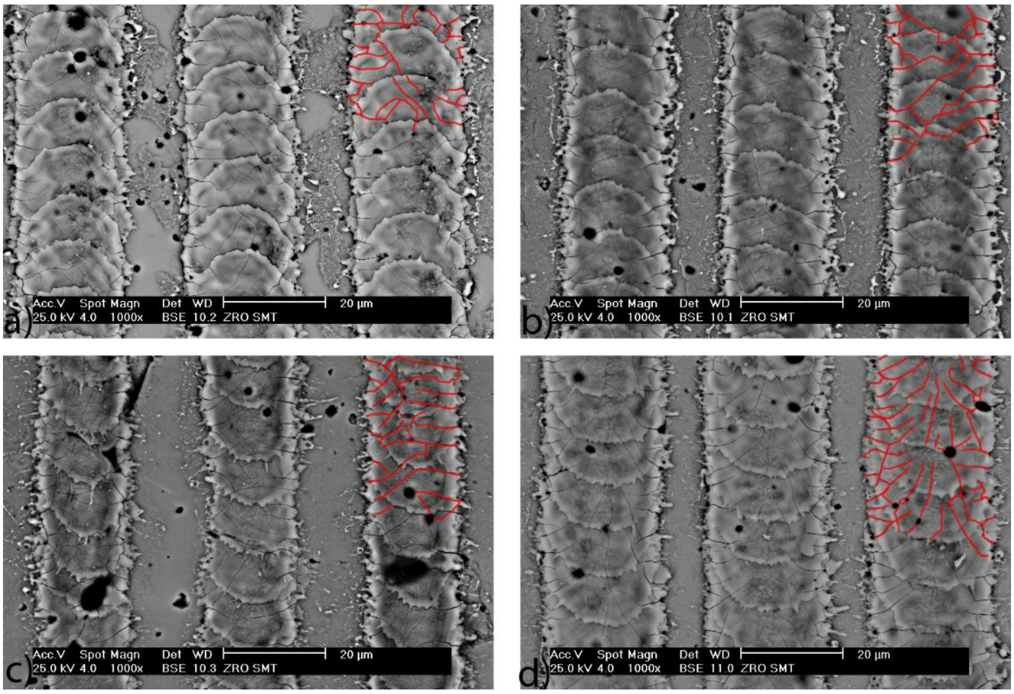

Figure 1. Samples 1-4. SEM analyses of the grooves from the surface.

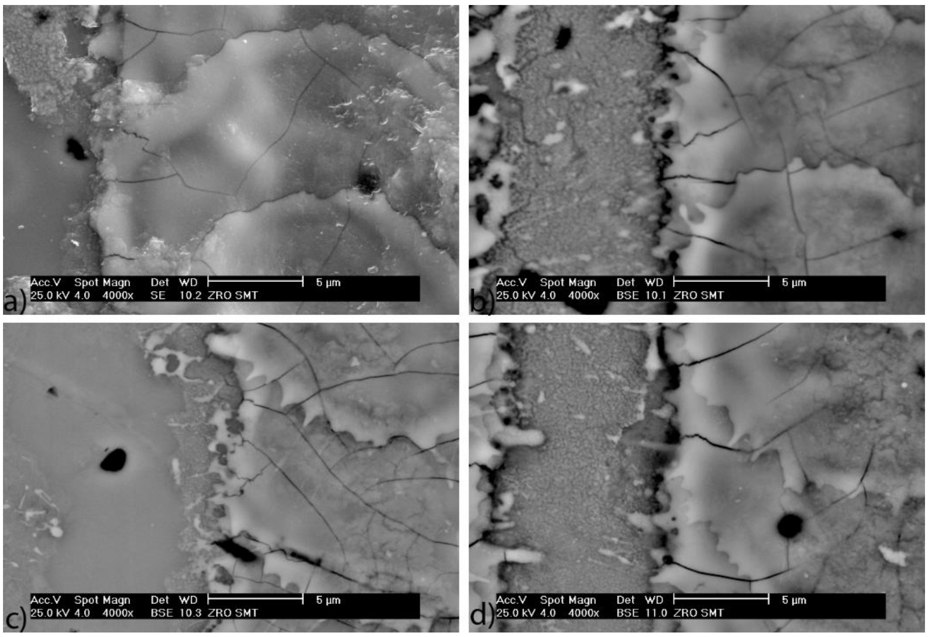

Figure 2. High magnification figures of the samples 1-4.

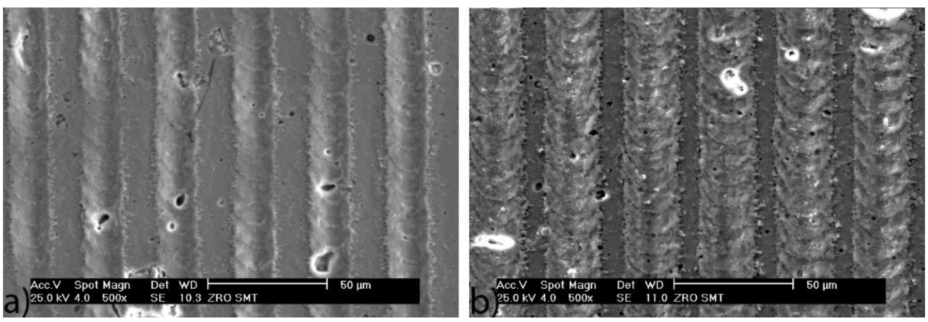

Figure 3. Microscope images of 15µJ(a) and 45µJ(b) made grooves.

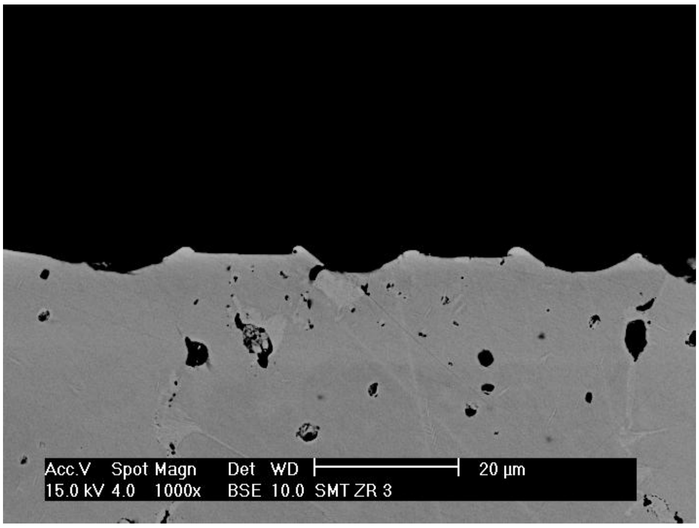

Figure 4. Cross-section cut of sample 3.

	1	2	3	4	5
Element	Wt %	Wt %	Wt %	Wt %	Wt %
O K	11.94	13.35	12.44	11.98	11.31
MgK	1.73	1.53	2.14	2.02	2.51
HfM	2.71	2.59	5.24	4.93	5.39
ZrK	83.62	82.53	80.17	81.06	80.79
Total	100	100	100	100	100

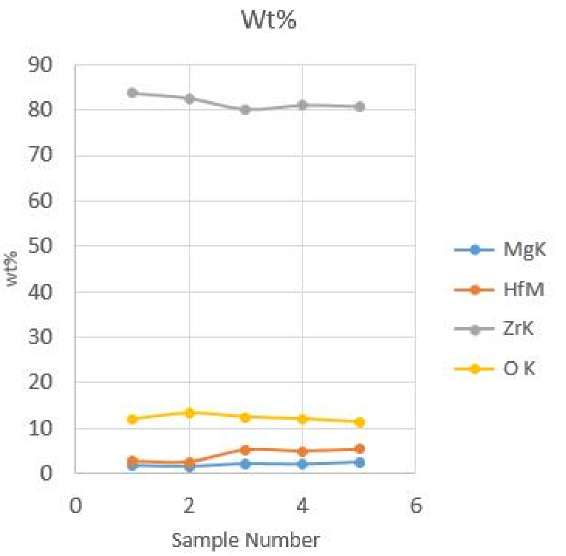

Figure 5. Wt% of sample 1-4 and reference sample 5.

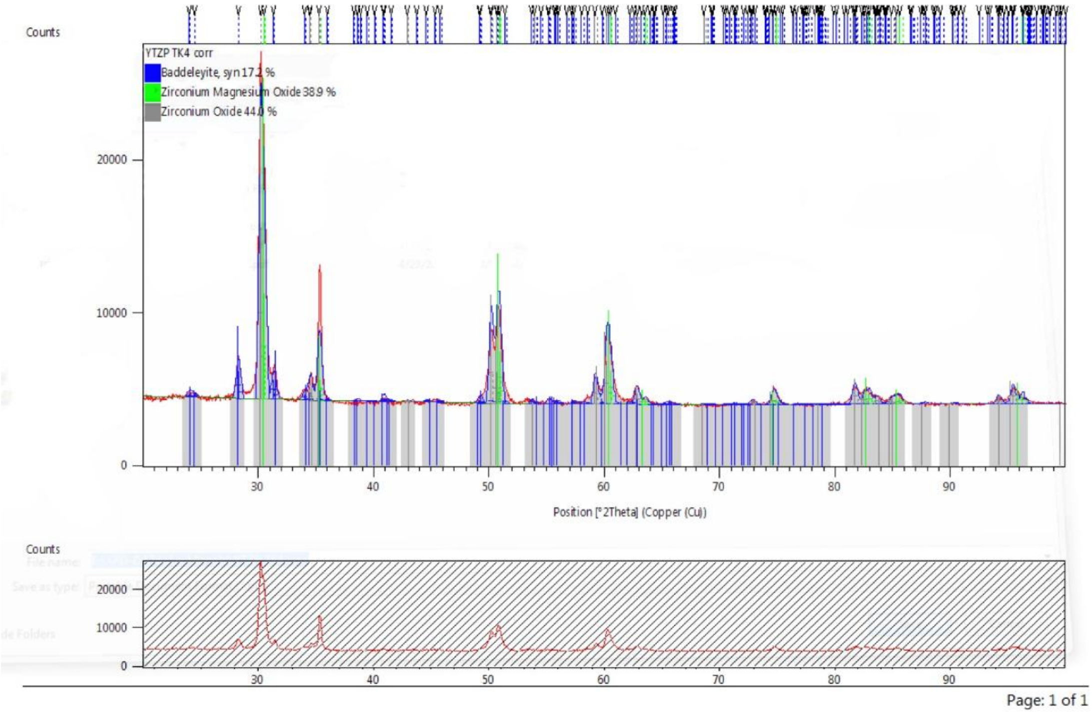

Figure 6. XRD-analyse from the sample 4.

Table 1. Process parameters for the samples

Sample	Pulse energy [µJ]	Speed [mm/s]	Wavelength [nm]	Repetitions
S1	45	100	515	2x
S2	30	100	515	4x
S3	15	100	515	6x
S4	45	100	515	3x
S5	Polished reference sample – No laser treatment			
S6	Untreated reference sample – No laser treatment			
S7	100	100	1030	1x
S8	100	100	1030	1x

Table 2. XRD-analyses of samples.

	S1	S4	S6	S5 Polished	S6 Untreated	S8 Polished	S8 Untreated
Monoclinic	17.6	17.1	14.8	21.7	43.7	12.8	12.8
Tetragonal	39.6	38.9	39.5	32.0	25.7	40.2	39.1
Cubic	42.8	44.0	45.7	46.3	30.6	47.0	48.1
Total percent	100	100	100	100	100	100	100