

ZrB<sub>2</sub>-SiC COMPOSITES WITH RARE-EARTH OXIDE ADDITIVES

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**Abstract:** The effect of different content (2, 5, and 10 wt.%) of two different types of rare earth (RE) oxides (Eu<sub>2</sub>O<sub>3</sub> and Lu<sub>2</sub>O<sub>3</sub>) on the sintering, microstructure, room temperature mechanical properties, and ablation resistance of ZrB<sub>2</sub>-25vol.% SiC ceramics were investigated. The materials were prepared using non-reactive Field Assisted Sintering Technology (FAST) in the temperature range of 1950°C – 2050°C, with a pressure of 70 MPa and a dwell of 7 min. No significant effect of the addition of 2 and 5 wt.% RE<sub>2</sub>O<sub>3</sub> on the microstructure and the room temperature mechanical properties (hardness, indentation fracture toughness, and flexural strength) were observed. On the other hand, the coarser microstructures led to the deterioration of flexural strength and the hardness of the composites sintered with 10 wt.% RE<sub>2</sub>O<sub>3</sub>. The ablation resistance of the materials (tested up to ~ 2670°C) gradually increased with the increasing amount of RE oxides. The material with 10 wt.% Lu<sub>2</sub>O<sub>3</sub> showed the best ablation resistance among all of the investigated compositions, with more than two times a lower ablation rate than that of the reference ZrB<sub>2</sub>-25vol.%SiC.

Keywords: ultra-high temperature ceramics; zirconium diboride; rare-earth additives; mechanical properties; ablation resistance

## 1. Introduction

Zirconium diboride (ZrB<sub>2</sub>), similar to other so-called Ultra-High Temperature Ceramics (UHTC), has a high melting temperature (above 3000°C), good thermal and electric conductivity, good oxidation resistance and strength at elevated temperatures [1]. Such materials are used for applications performing at high temperatures, such as rocket propulsion, or thermal protection system for sharp leading edges of hypersonic vehicles [1, 2]. Although ZrB<sub>2</sub> has an extremely high melting temperature (3246°C), monolithic ZrB<sub>2</sub> has limited oxidation resistance [3, 4], as during oxidation in the air above 1000°C, B<sub>2</sub>O<sub>3</sub> (one of the oxidation products of ZrB<sub>2</sub>) starts evaporating, and the porous ZrO<sub>2</sub> layer (second oxidation product of ZrB<sub>2</sub>) is the only phase remaining after the oxidation above 1500°C [5]. In addition, the phase transformation of ZrO<sub>2</sub> (1000-1200°C) leads to the volume change and the increased porosity of the layer, which significantly accelerates the oxidation rate [6].

Silicon carbide (SiC) is one of the most commonly used additives to improve the oxidation resistance of monolithic ZrB<sub>2</sub> ceramics. During oxidation, it forms a borosilicate glass on the surface of ZrB<sub>2</sub>-SiC, which reduces oxygen permeation [1]. For this reason, ZrB<sub>2</sub> - SiC composites have been considered the most promising material systems for ultra-high-temperature environments [7]. However, the borosilicate layer can be protective only in a non-air-flowing atmosphere. Under the action of strong heat flux and high pressure, the formed silica may volatilize quickly and be blown away by high-speed airflow, leaving porous ZrO<sub>2</sub> on the surface of materials [8]. Since new materials for hypersonic applications need to meet the strict requirements of the aerospace industry to withstand temperatures above 2000°C, the further improvement of oxidation/ablation resistance of ZrB<sub>2</sub>-based ceramics is still one of the most important challenges to broaden their application potential.

Therefore, the aim of the work was to investigate the effect of various amounts (2, 5, and 10 wt.%) of rare-earth oxide additives (Eu<sub>2</sub>O<sub>3</sub>, Lu<sub>2</sub>O<sub>3</sub>) on the mechanical properties of ZrB<sub>2</sub>-25vol.%SiC materials, including their ablation resistance. It is well known that the refractoriness of the rare-earth oxides increases with the increasing cation field strength, which increases with the decreasing ionic radius of RE<sup>3+</sup> (i.e. with the increasing atomic number in the periodic table) [9]. Therefore, Lu<sub>2</sub>O<sub>3</sub> was chosen

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as the rare-earth with the smallest radius of  $RE^{3+}$  [10], while its effect on the properties of  $ZrB_2$ -based ceramics was compared to the effect of RE from the middle of the lanthanide group ( $Eu_2O_3$ ).

## 2. Experimental procedure

Commercially available powders of  $ZrB_2$  (d50 ~1.5-3.0  $\mu m$ , grade B, H.C. Starck),  $\beta$ -SiC (d50 ~0.6  $\mu m$  Superior Graphite,  $\beta$ -SiC), and rare earth oxides, such as  $Eu_2O_3$  and  $Lu_2O_3$ , (d50 ~3.0-15.0  $\mu m$ , Treibacher,) were used as the raw materials. The  $ZrB_2$ /SiC ratio was kept constant (75 vol.%  $ZrB_2$ /25 vol.% SiC), while the amount of rare-earth oxides was 2, 5, or 10 wt.%. The powder mixtures were prepared by a planetary ball mill (Retsch PM 100) using tungsten carbide (WC) milling media and isopropanol as the solvent. The rotation speed and the milling time were 150 rpm and 6 h, respectively. The reference  $ZrB_2$ -25vol.%SiC sample without rare-earth sintering additives was also prepared for the sake of comparison.

The dried milled powders were uniaxially pressed in a graphite die with a diameter of 20 mm at a pressure of 30 MPa. The sintering was performed using Field Assisted Sintering Technology (DSP 507, Dr. Fritsch GmbH.) at the temperature range of 1950-2050°C and the pressure of 70 MPa in Argon atmosphere. Both the heating and cooling rates were 100°C/min, while the dwell time was 7 minutes. The density was measured by the Archimedes method.

The microstructures of the materials were investigated using SEM (AURIGA Compact, Zeiss). The crystalline phases were identified using X-ray diffraction (Panalytical Empyrean, Cu  $K\alpha$  radiation), followed by the Rietveld analysis using HighScore Plus software. The hardness and the indentation fracture toughness were evaluated using a Vickers indentation (ZWICK ROELL Z2.5), at the load of 9.81 N. The indentation fracture toughness was calculated using the formula proposed by Anstis et al. [11]. The ablation resistance of the materials was investigated by an oxyacetylene flame up to the maximum temperature of about 2660°C, measured on the surface of the materials by an optical pyrometer. The distance between the torch nozzle and the sample was 15 mm. While keeping the distance between the nozzle and the sample constant, the gas flows were changed in three steps with the  $C_2H_2:O_2$  ratio of 1.2:1.5, 3:4, and 8:12 L/min. The dwell time at the maximum temperature was 60 s. The ablated surfaces of the specimens were observed using a confocal microscope (Lext OLS 3100, Olympus) to determine the maximum depth of the ablated zone. The maximum depth was then used to calculate the linear ablation rates of the materials when divided by the dwell time at the maximal temperature (60 s).

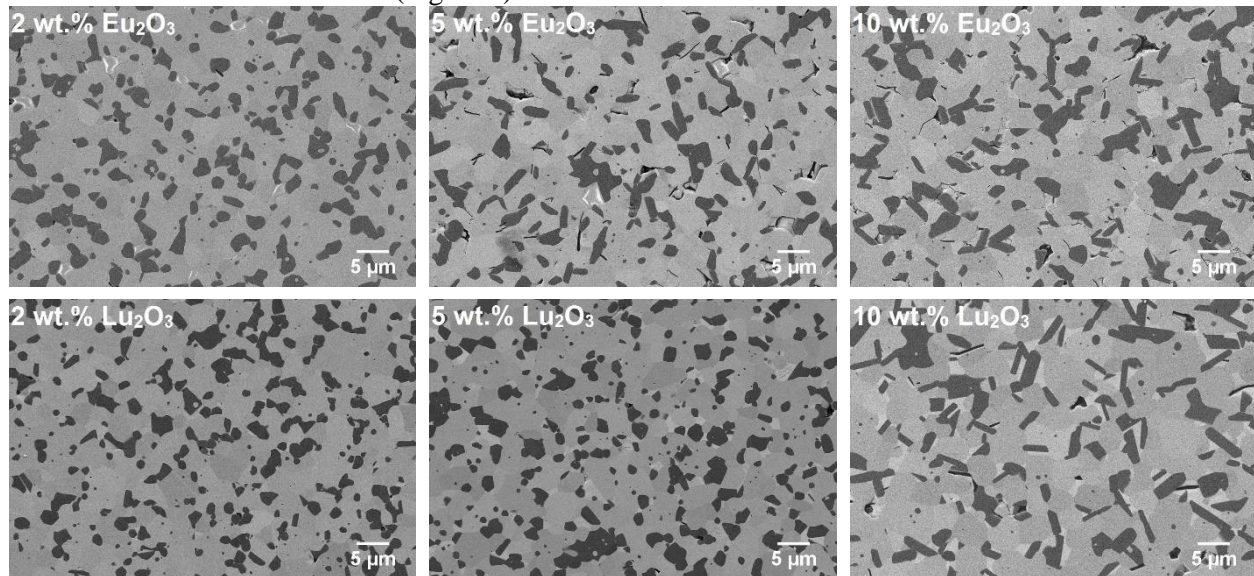
## 3. Results and discussions

### a. Microstructure analysis

The addition of both  $Eu_2O_3$  and  $Lu_2O_3$  significantly improved the densification of  $ZrB_2$ -ceramics. While the temperature of 2050°C was necessary to use to obtain near-fully dense reference  $ZrB_2$ -25vol.% SiC materials, the maximum sintering temperature could be lowered to 2000°C after the addition of 2 and 5 wt.%  $RE_2O_3$  to obtain the materials with similar relative densities (> 98 wt.%). The addition of 10 wt.% RE oxides further enhanced densification, and near-fully dense materials were obtained at an even lower temperature (1950°C) when compared to the materials with 2 and 5 wt.%  $RE_2O_3$  (2000°C) or the reference  $ZrB_2$ -SiC sample (2050°C). It should be pointed out that when the  $ZrB_2$ -SiC composites with 10 wt.%  $RE_2O_3$  were sintered at temperatures above 1950°C, and the formation of a liquid phase coming out of the die was observed during sintering.

Using the optimized sintering parameters, all of the materials were near-fully dense, having relative densities above 98 % (Table 1). The SEM analysis of the microstructures revealed the presence of uniformly distributed SiC particles (dark grey phase in Figure 1) in the  $ZrB_2$  matrix (light grey phase in Figure 1). The materials sintered with  $Lu_2O_3$  contained a less number of pores when compared to the materials with  $Eu_2O_3$ , which corresponds well to the relative densities of the samples. The number of elongated SiC grains increased with the increasing amount of additives, and they became predominant when 10 wt.% additives were used. This suggests that the phase transformation of SiC grains occurred during sintering, as a consequence of the presence of a greater amount of a liquid phase ( $RE_2O_3$ ), which always promotes the phase transformation of SiC [12, 13]. The greater amount of the liquid phase also promoted grain growth during sintering, leading to the significantly coarser

microstructures of the composite sintered with 10 wt.% RE oxides when compared to the materials with 5 wt.% or 2 wt.% additives (Figure 1).

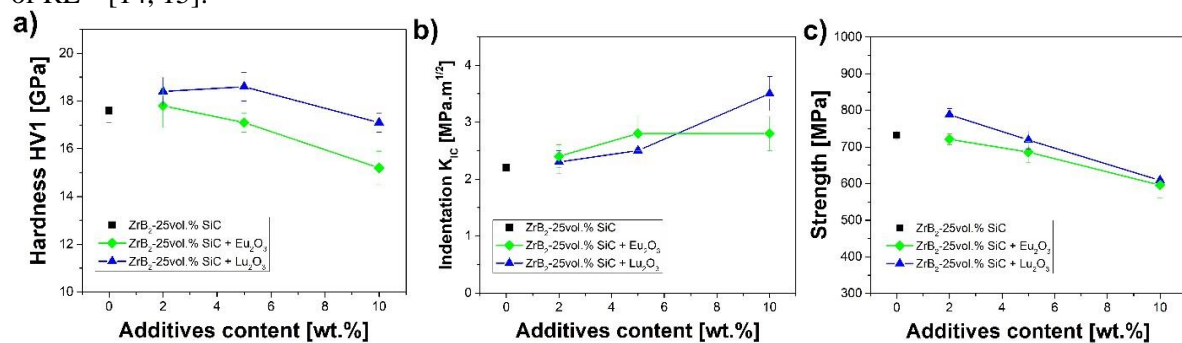


**Figure 1.** SEM microstructures of  $ZrB_2$ -25vol.%SiC composites sintered with different types and amounts of  $RE_2O_3$ .

### b. Room temperature mechanical properties

The room temperature mechanical properties of the reference  $ZrB_2$ -25vol.%SiC material and the  $ZrB_2$ -25vol.%SiC composites with different content of RE oxides, such as hardness, indentation fracture toughness, and flexural strength, are given in Figure 2a, 2b, and 2c, respectively. In general, the hardness and strength of the materials decreased with the increasing amount of additives, while the indentation fracture toughness increased. However, it can be concluded that no significant effect of the addition of 2 wt.% and 5 wt.% RE oxides on the room temperature mechanical properties of the composites was observed, as the values were similar to those measured for the reference  $ZrB_2$ -25vol.%SiC sample without RE oxides. On the other hand, the addition of 10 wt.% RE oxides resulted in a more significant effect on the mechanical properties of  $ZrB_2$ -25vol.%SiC composites. The significantly coarser microstructures of the composites with 10 wt.%  $RE_2O_3$  led to the deterioration of both the hardness and the strength of the materials. On the contrary, the presence of larger  $ZrB_2$  grains and the elongated SiC grains resulted in the increased indentation fracture toughness of the samples with 10 wt.%  $RE_2O_3$ .

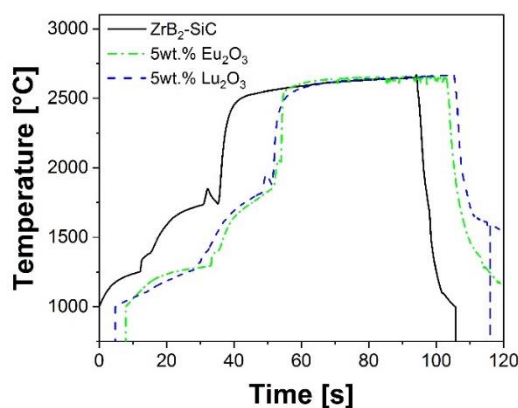
Although no significant difference between the mechanical properties of  $ZrB_2$ -25vol.%SiC sintered with  $Eu_2O_3$  and  $Lu_2O_3$  additives was observed, still the composites sintered with  $Lu_2O_3$  exhibited slightly better room temperature mechanical properties (Figure 2). This can be attributed either to the higher relative density of the composites sintered with  $Lu_2O_3$  additive or to the higher cationic field strength (CFS) of the Lu-based grain boundary phase, which increases with a decreasing ionic radius of  $RE^{3+}$  [14, 15].



**Figure 2.** Hardness (a), indentation fracture toughness (b), and strength (c) of  $ZrB_2$ -25vol.%SiC composites sintered with different content of  $RE_2O_3$  (RE = Eu, or Lu).

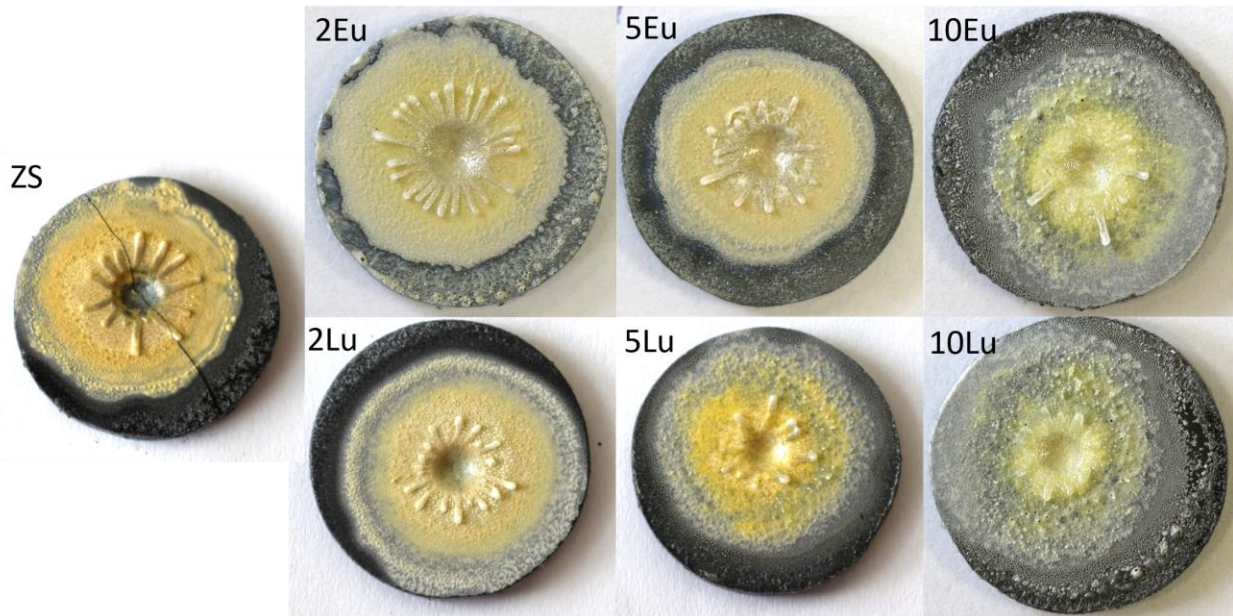
**c. Ablation resistance**

The high-temperature properties of the materials were evaluated in terms of the ablation tests up to the temperature of  $\sim 2600^{\circ}\text{C}$  using an oxyacetylene flame. Figure 3 shows the examples of temperature profiles recorded during the test of the reference  $\text{ZrB}_2\text{-25vol.\%SiC}$  system and the composites sintered with 5wt.%  $\text{Eu}_2\text{O}_3$  and  $\text{Lu}_2\text{O}_3$ . The maximum temperature was reached within the three steps, while each step corresponded to the change of the gas flows, as described in the experimental procedure part. It should be pointed out that the materials were exposed to the extremely rapid heating of  $\sim 90^{\circ}\text{C/s}$ , as in the final stage the temperature measured on the surface of the samples raised from  $\sim 1800^{\circ}\text{C}$  to  $\sim 2500^{\circ}\text{C}$  within approximately 8 s, followed by a slight steady increase of the temperature up to  $\sim 2670^{\circ}\text{C}$  during the dwell of 60 s. Besides the extreme heating rate, the samples were also exposed to rapid cooling with a rate of  $180\text{-}200^{\circ}\text{C/s}$ . Figure 3 also demonstrates that all the materials were tested at the same conditions.



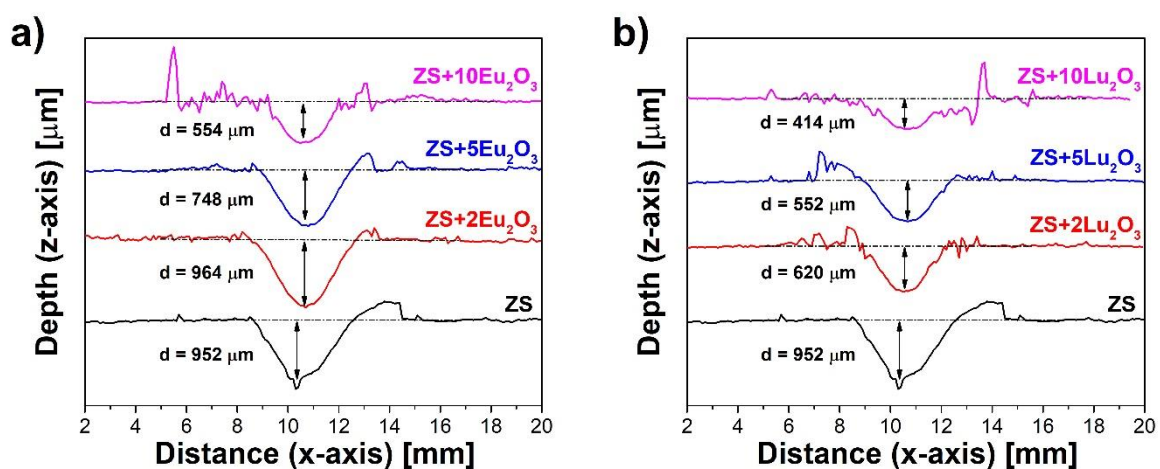
**Figure 3.** Temperature profile recorded during the oxyacetylene ablation test of the reference  $\text{ZrB}_2\text{-25vol.\%SiC}$  material and the  $\text{ZrB}_2\text{-25vol.\%SiC}$  composites sintered with 5 wt.%  $\text{Eu}_2\text{O}_3$  and  $\text{Lu}_2\text{O}_3$ .

The macro-images of the surfaces of the samples after the ablation test are shown in Figure 4. The reference  $\text{ZrB}_2\text{-25vol.\%SiC}$  sample was the only composition that cracked upon cooling from the maximum temperature. All of the other samples survived harsh testing conditions without cracking. The surface of the specimens was covered by a yellowish oxide layer, and the central part of the samples showed a significant ablation. Since the nozzle of the oxyacetylene torch was aimed at the center of the samples, both the maximum temperature and the maximum gas pressure resulted in the melting and splashing of the material from the central region. However, both the ablation and the splashing became less significant with the increase of the additive content (Figure 4).



**Figure 4.** Macro-images of the surface of the  $\text{ZrB}_2\text{-25vol.\%SiC}$  materials with different types and content of the additives after the oxyacetylene ablation test at  $\sim 2670^\circ\text{C}$  for 60 s. All of the samples had a diameter of 20 mm.

The maximum height profiles of the ablated materials, determined by confocal microscopy, are given in Figure 5. The maximum ablated depth continuously decreased with the increasing amount of both  $\text{Eu}_2\text{O}_3$  (Figure 5a) and  $\text{Lu}_2\text{O}_3$  (Figure 5b) additives. In other words, the higher the content of the RE oxides the better the ablation resistance of the materials. The maximum ablated depth was then used to determine the linear ablation rates of the individual materials, which are summarized in Table 1. The lowest maximum ablated depth (so the lowest linear ablation rate) was observed for the  $\text{ZrB}_2\text{-25vol.\%SiC}$  sintered with 10 wt.%  $\text{Lu}_2\text{O}_3$ , which was more than two times lower than that of the reference  $\text{ZrB}_2\text{-25vol.\%SiC}$  material without any RE oxides. More importantly, the material containing 5 wt.%  $\text{Lu}_2\text{O}_3$  exhibited a similar maximum ablated depth (Figure 5) and the linear ablation rate (Table 1) as measured for the composite with 10 wt.%  $\text{Eu}_2\text{O}_3$ . This suggests the superior effect of the  $\text{Lu}_2\text{O}_3$  additive on the improvement of ablation resistance of  $\text{ZrB}_2\text{-25vol.\%SiC}$  materials over the effect  $\text{Eu}_2\text{O}_3$  additive.

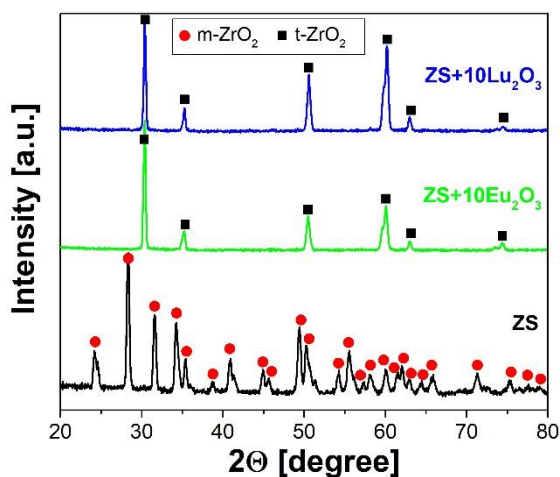


**Figure 5.** Maximum height profiles of the  $\text{ZrB}_2\text{-25vol.\%SiC}$  materials with different content of a)  $\text{Eu}_2\text{O}_3$  and b)  $\text{Lu}_2\text{O}_3$  additives after the oxyacetylene ablation test at  $\sim 2670^\circ\text{C}$  for 60 s.

**Table 1.** Relative densities, and linear ablation rates of ZrB<sub>2</sub>-25vol.%SiC materials with different types (Eu<sub>2</sub>O<sub>3</sub> and Lu<sub>2</sub>O<sub>3</sub>) and content (2, 5, and 10 wt.%) of additives after the oxyacetylene ablation test at ~ 2660°C for 60 s.

Material composition	Relative density [%]	Linear ablation rate [mm/s]
ZrB <sub>2</sub> -25vol.%SiC	98.8	15.9 x 10 <sup>-3</sup>
ZrB <sub>2</sub> -25vol.%SiC+2wt.%Eu <sub>2</sub> O <sub>3</sub>	99.0	16.1 x 10 <sup>-3</sup>
ZrB <sub>2</sub> -25vol.%SiC+5wt.%Eu <sub>2</sub> O <sub>3</sub>	98.1	12.5 x 10 <sup>-3</sup>
ZrB <sub>2</sub> -25vol.%SiC+10wt.%Eu <sub>2</sub> O <sub>3</sub>	98.5	9.2 x 10 <sup>-3</sup>
ZrB <sub>2</sub> -25vol.%SiC+2wt.%Lu <sub>2</sub> O <sub>3</sub>	99.3	10.3 x 10 <sup>-3</sup>
ZrB <sub>2</sub> -25vol.%SiC+5wt.%Lu <sub>2</sub> O <sub>3</sub>	99.8	9.2 x 10 <sup>-3</sup>
ZrB <sub>2</sub> -25vol.%SiC+10wt.%Lu <sub>2</sub> O <sub>3</sub>	98.9	6.9 x 10 <sup>-3</sup>

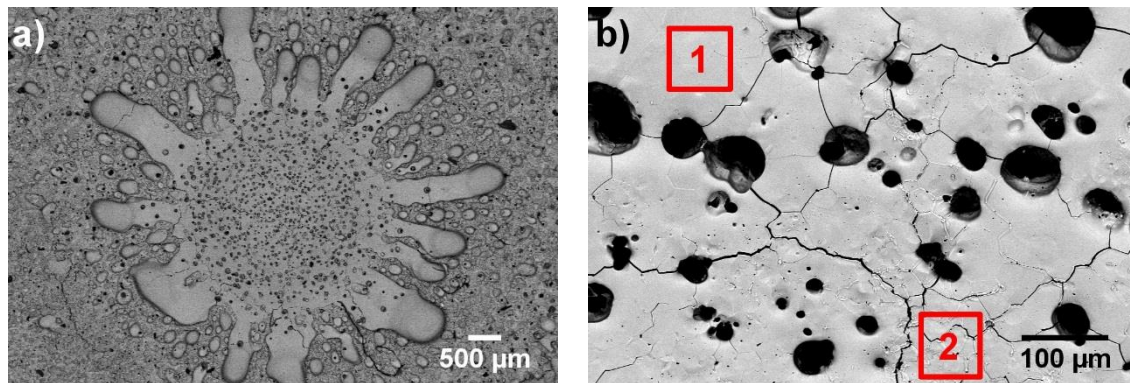
The XRD patterns of the surfaces of the reference sample and the composites sintered with 10 wt.% RE<sub>2</sub>O<sub>3</sub> after the ablation test by oxyacetylene flame at ~ 2670°C for 60 s are shown in Figure 6. While the oxide layer of the reference ZrB<sub>2</sub>-25vol.%SiC sample was composed of monoclinic ZrO<sub>2</sub> phase (m-ZrO<sub>2</sub>) only, tetragonal ZrO<sub>2</sub> (t-ZrO<sub>2</sub>) was detected for the samples with 10 wt.% Eu<sub>2</sub>O<sub>3</sub> and Lu<sub>2</sub>O<sub>3</sub>. This suggests the presence of RE<sub>2</sub>O<sub>3</sub> in the microstructure of the base ZrB<sub>2</sub>-25vol.% SiC material had a stabilizing effect to prevent the phase transformation of monoclinic ZrO<sub>2</sub> in the oxide layer upon cooling from the maximum temperature during the ablation test.



**Figure 6.** XRD patterns of the surfaces of ZrB<sub>2</sub>-25vol.%SiC material and ZrB<sub>2</sub>-25vol.%SiC sintered with 10 wt.% Eu<sub>2</sub>O<sub>3</sub> and Lu<sub>2</sub>O<sub>3</sub> additives after the oxyacetylene ablation test at ~ 2670°C for 60 s.

The back-scattered SEM images of the top surface of ZrB<sub>2</sub>-25vol.%SiC with 10 wt.% Lu<sub>2</sub>O<sub>3</sub> additive after the oxyacetylene ablation test is shown in Figure 7. Besides the presence of a few pores, the surface was covered by a compact oxide layer. The EDS analysis (not shown here) confirmed the presence of Zr and O<sub>2</sub> as the major elements in the oxide layer (in good agreement with the XRD results), while a small amount of Lu was also detected. Interestingly, the Lu element was homogenously distributed throughout the oxide layer without any significant concentration gradient observed (e.g. the concentration of Lu was 1.4 at.% and 1.2 at.% when detected in two different areas, shown as 1 and 2 in Figure 7b, respectively). Since no separated Lu-containing phases were observed in the oxide layer, the present results suggest that the formation of Lu-ZrO<sub>2</sub> solid solution occurred during the ablation test. This led to the stabilization of a high-temperature tetragonal modification of ZrO<sub>2</sub>. The same effect is well known for the Y element in the commercially available Y-stabilized ZrO<sub>2</sub>, and a similar stabilizing effect was recently reported for the ZrB<sub>2</sub>-xSiC composites (x = 5, 10, 15, 18.5 vol.%) sintered with 5 wt.% Y<sub>2</sub>O<sub>3</sub> [16]. The stabilization of t-ZrO<sub>2</sub> had a clear positive effect on the improvement of ablation resistance of ZrB<sub>2</sub>-SiC materials, as the materials with 10 wt.% RE<sub>2</sub>O<sub>3</sub> showed significantly lower ablation rates when compared to the reference material without any RE oxide additives.

Although the addition of both additives ( $\text{Eu}_2\text{O}_3$  and  $\text{Lu}_2\text{O}_3$ ) led to the stabilization of tetragonal  $\text{ZrO}_2$ , still the materials sintered with  $\text{Lu}_2\text{O}_3$  showed a superior ablation resistance over the  $\text{Eu}_2\text{O}_3$  additive. This can be explained by higher refractoriness of  $\text{Lu}_2\text{O}_3$ , as it is well known that the viscosity of RE-containing phases increases with a decreasing ionic radius of  $\text{RE}^{3+}$ . The increased viscosity then slows down the diffusion rate of oxygen through the protective surface oxide layer [9]. Therefore, the superior ablation resistance of  $\text{ZrB}_2$ -25vol.%SiC sintered with  $\text{Lu}_2\text{O}_3$  can be attributed to the fact that the  $\text{Lu}_2\text{O}_3$  additive has the smallest ionic radius ( $\text{Lu}^{3+}$ ) among all of the RE oxides. A direct effect of the cation size of RE on the improvement of oxidation resistance was already reported for  $\text{Si}_3\text{N}_4$ -based ceramics [9], and the positive effect of RE oxides with a small  $\text{RE}^{3+}$  on the improvement of ablation/oxidation resistance of  $\text{ZrB}_2$ -SiC was clearly demonstrated in the present work. In order to reveal a clear mechanism, more detailed investigations, including SEM of cross-sections of the oxide layers and TEM analysis of the oxide layers will be carried out in the near future.



**Figure 7.** a) Back-scattered SEM images of the top surface of  $\text{ZrB}_2$ -25vol.%SiC with 10 wt.%  $\text{Lu}_2\text{O}_3$  additive after the oxyacetylene ablation test at  $\sim 2660^\circ\text{C}$  for 60 s; b) a higher magnification of the central part of the ablated zone.

#### 4. Conclusions

Near-fully dense  $\text{ZrB}_2$ -25vol.%SiC with different content (2, 5, and 10 wt.%) of  $\text{Eu}_2\text{O}_3$  and  $\text{Lu}_2\text{O}_3$  additives were successfully prepared using the non-reactive FAST process at the temperature of  $1950^\circ\text{C} - 2050^\circ\text{C}$ , and the pressure of 70 MPa. The following main conclusions can be made:

- The addition of RE oxides significantly improved the densification of  $\text{ZrB}_2$ -SiC, and the sintering temperature was lowered from  $2050^\circ\text{C}$  to  $1950^\circ\text{C}$  when 10 wt.%  $\text{RE}_2\text{O}_3$  was used.
- Both the hardness and the flexural strength of the materials decreased with the increasing amount of  $\text{RE}_2\text{O}_3$ , while the indentation fracture increased. The materials with  $\text{Lu}_2\text{O}_3$  showed slightly better room temperature mechanical properties because of their higher relative density and a higher cation field strength of the grain boundary phase.
- In general, no significant effect of RE oxides on the room temperature mechanical of  $\text{ZrB}_2$ -25vol.%SiC was observed up to 5 wt.%  $\text{RE}_2\text{O}_3$ . The coarser microstructures in the case of materials with 10 wt.%  $\text{RE}_2\text{O}_3$  resulted in a more significant deterioration of the hardness and strength of the materials.
- The ablation resistance significantly increased with the increasing amount of  $\text{RE}_2\text{O}_3$  additives. The addition of RE oxides stabilized the high-temperature tetragonal modification of  $\text{ZrO}_2$  in the oxide layer.
- The material sintered with 10 wt.%  $\text{Lu}_2\text{O}_3$  showed the best ablation resistance among all of the investigated compositions, as its linear ablation rate was more than two times lower ( $6.9 \times 10^{-3} \text{ mm/s}$ ) when compared to the reference  $\text{ZrB}_2$ -SiC without any RE additives ( $15.9 \times 10^{-3} \text{ mm/s}$ ).

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