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High-temperature oxidation of ZrB_2–SiC–La_2O_3 ceramic material produced via spark plasma sintering

V. B. Kulmetyeva, V. E. Chuvashov, K. N. Lebedeva, S. E. Porozova ✉, M. N. Kachenyuk

Perm National Research Polytechnic University
29 Komsomolsky Prosp., Perm 614000, Russia

✉ sw.porozova@yandex.ru

Abstract. The study investigated the influence of La_2O_3 addition on the oxidation properties of composite ceramics with a composition of 80 vol. % ZrB_2 and 20 vol. % SiC. The source materials utilized in this study included zirconium diboride (DPTP Vega LLC., Russia), grade 63C silicon carbide (Volzhsky Abrasive Works JSC, Russia), and lanthanum hydroxide concentrate (Solikamsk Magnesium Plant JSC, Russia), with the following elemental content (wt. %): La – 54.2, Nd – 4.3, Pr – 2.8, and trace amounts of other elements (<0.1). The La_2O_3 content in the charge varied between 0, 2 and 5 vol. %. The powders were mixed in a planetary mill with ethyl alcohol as the medium for 2 h, using a grinding media to powder ratio of 3:1. Consolidation of the powders was achieved through spark plasma sintering at 1700 °C, applying a pressing pressure of 30 MPa. The heating rate was 50 °C/min, and the isothermal holding time was 5 min. Oxidation was carried out in air at 1200 °C and the total oxidation time was 20 h. Oxidation experiments were conducted in air at 1200 °C, with a total oxidation time of 20 h. It was observed that the most significant weight gain occurred within the first 2–4 h of testing. Specimens containing 5 vol. % La_2O_3 exhibited the smallest weight gain after 20 h of exposure. Regardless of the presence of La_2O_3, silicon carbide was found to be the first material to undergo oxidation. In specimens without La_2O_3 addition, the oxidized layer mainly consisted of silicon monoxide and dioxide. In contrast, specimens with La_2O_3 exhibited a predominantly oxidized layer composed of $ZrSiO_4$ and ZrO_2. The study revealed that the introduction of La_2O_3 intensified the formation of zircon, which subsequently slowed down the oxidation processes in the material.

Keywords: oxidation, spark plasma sintering, zirconium diboride, silicon carbide, lanthanum oxide, oxidized layer, energy dispersive analysis, elemental composition

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Особенности высокотемпературного окисления керамического материала ZrB_2–SiC–La_2O_3, полученного искровым плазменным спеканием

В. Б. Кульметьева, В. Э. Чувашов, К. Н. Лебедева, С. Е. Порозова ✉, М. Н. Каченюк

Пермский национальный исследовательский политехнический университет
Россия, 614000, г. Пермь, Комсомольский пр-т, 29

✉ sw.porozova@yandex.ru

Аннотация. Исследовано влияние добавки La_2O_3 на окисление керамики состава, об. %: 80ZrB_2–20SiC. В качестве исходных материалов использовали диборид циркония (ООО ДПТП «Вега», Россия), карбид кремния марки 63С (ОАО «Волжский

абразивный завод», Россия) и концентрат гидроксида лантана (ОАО «Соликамский магниевый завод», Россия), содержание элементов в котором составляло, мас. %: La – 54,2, Nd – 4,3, Pr – 2,8, остальные – менее 0,1. Содержание La_2O_3 в шихте варьировалось: 0, 2 и 5 об. %. Смешивание порошков проводили с использованием планетарной мельницы в течение 2 ч в этиловом спирте, соотношение мелющих тел и порошка составляло 3:1. Консолидацию порошков осуществляли методом искрового плазменного спекания при температуре 1700 °С и давлении прессования 30 МПа со скоростью нагрева 50 °С/мин и изотермической выдержкой 5 мин. Окисление проводили на воздухе при температуре 1200 °С, общее время окисления составило 20 ч. Наиболее интенсивное увеличение массы отмечено в течение первых 2–4 ч испытаний. По истечении 20 ч наименьшее увеличение массы наблюдалось у образцов с добавкой 5 об. % La_2O_3. Установлено, что вне зависимости от наличия La_2O_3 карбид кремния первым подвергается окислению. В образцах без добавки La_2O_3 окисленный слой состоит преимущественно из моно- и диоксида кремния, тогда как в образцах с La_2O_3 большую часть окисленного слоя составляют $ZrSiO_4$ и ZrO_2. Таким образом, установлено, что введение La_2O_3 интенсифицирует процесс формирования циркона, что способствует замедлению процессов окисления.

Ключевые слова: окисление, искровое плазменное спекание, диборид циркония, карбид кремния, оксид лантана, окисленный слой, энергодисперсионный анализ, элементный состав

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Introduction

To date, the primary concern lies in the development of materials capable of enduring extended periods in oxidizing environments at high temperatures [1–3]. In this regard, a noteworthy focus is on ultra-high-temperature ceramics (UHTC), which consist of a ceramic matrix and a protective structure that shields the surface from oxidation [1; 4; 5]. In order to produce such materials a deliberate selection of additive phases is conducted to facilitate the formation of surface structures that can withstand prolonged exposure to oxidizing environments at high temperatures. One prevalent example of UHTCs is composite materials based on zirconium or hafnium borides, which exhibit high thermal conductivity and thermal shock resistance [6].

Sintering zirconium and hafnium boride powders requires temperatures exceeding 1950 °C due to their strong covalent bonds and low self-diffusion coefficient [7; 8]. The sintering process is typically activated by incorporating sintering additives such as SiC, Si_3N_4, La_2O_3, LaB_6 [9; 10], tantalum, titanium, zirconium, molybdenum silicides, etc. The optimum composition is considered to be the volumetric ratio of 80 % ZrB_2 to 20 % SiC [11; 12]. At high temperatures, the oxidation of these ceramics leads to the formation of a protective multi-layer coating on the surface, consisting of ZrO_2–SiO_2 and borosilicate glass. This coating effectively seals cracks and pores on the UHTC surface, creating a gas-tight film that prevents oxygen diffusion into the material [13; 14].

Spark plasma sintering (SPS) is a relatively recent technique that enables the reduction of sintering temperature and time for certain materials when performed under vacuum or an argon atmosphere [15]. Despite some existing studies in this area, the phase composition, structure, and oxidation properties of boride-based composite materials produced through this process have not been adequately investigated [15–17].

The objective of this study was to examine the impact of La_2O_3 addition on the oxidation properties of composite ceramics with the following volumetric composition: 80ZrB_2–20SiC.

Materials and Methods of Research

The source materials utilized in this study included:

– zirconium diboride (DPTP Vega LLC., Russia);

– lanthanum hydroxide concentrate (Solikamsk Magnesium Plant JSC, Russia), with the following elemental content (wt. %): La – 54,2, Nd – 4,3, Pr – 2,8 and trace amounts of other elements (<0.1);

– grade 63C silicon carbide (Volzhsky Abrasive Works JSC, Russia).

The particle size distribution of the powders was determined using laser light diffraction with the Analysette 22 NanoTec plant (Fritsch GmbH, Germany). The ZrB_2 powder exhibited a predominant particle size range of 0.5 to 12 μm, with 97 % of particles measuring less than 11.1 μm, and an average particle size of 4.52 μm. The SiC powder demonstrated a bimodal particle size distribution, with an average particle size of 3.47 μm. The $La(OH)_3$ powder exhibited a wide particle size distribution, with an average particle size of 9.76 μm.

In order to convert lanthanum hydroxide into oxide, the material was subjected to annealing at 600 °C for a duration of 1 h in an air atmosphere. The initial powders were mixed using a SAND planetary mill in ethyl alcohol. The grinding process lasted for 2 h at a speed of 160 rpm, a grinding media to powder ratio of 3:1. The mixtures contained lanthanum oxide in two different volumetric percentages: 0, 2 and 5.

The specimens were consolidated using spark plasma sintering (SPS) on the Dr. Synter SPS-1050b equipment

(SPS Syntex, Japan) at a temperature of 1700 °C. Heating was achieved by applying a pulsed direct current at a rate of 50 °C per min. The temperature was monitored using an optical pyrometer placed on the outer side of the graphite matrix. The material was loaded into the system just before the heating process began, while maintaining a constant load at a pressure of 30 MPa. The applied load was removed after the completion of the heating phase. To prevent any undesirable reactions between the sintered powder, matrix, and punches, graphite paper was employed. Additionally, graphite felt was wrapped around the mold to minimize heat losses. The specimens were subjected to an isothermal holding time of 5 min.

The apparent density and open porosity of sintered specimens were analyzed following the guidelines outlined in GOST 2409-2014.

For the oxidation study, the specimens were exposed to air in an electric furnace equipped with silicon carbide heaters. The crucibles containing the specimens were placed in the furnace, preheated to 1200 °C. After a specific duration, the specimens were removed, weighed to record their weight, and then returned to the furnace. The total duration of high-temperature oxidation was 20 h.

The phase composition of the specimens was examined using Raman spectroscopy on a multifunction spectrometer SENTERRA (Bruker, Germany), with a laser wavelength of 532 nm. The acquired data were processed using the OPUS 6.5 software.

Microscopic analysis of the specimens was conducted using an analytical auto emission scanning electron microscope VEGA3 (TESCAN, Czech Republic). In order to determine the elemental composition, an Inca X-Act detector (Oxford Instruments Analytical, Great Britain) was employed for energy-dispersive analysis of the elemental composition of the materials.

Results and Discussion

The investigations were conducted on the materials containing 0, 2 and 5 vol. % of La_2O_3. No significant changes in the apparent density and open porosity of the specimens were observed after the SPS process. The open porosity values ranged from 3.5 to 5.5 % across all variations.

The specimens were subjected to oxidation in an air environment for a duration of 20 h. The time intervals for recording the specific weight gain of the specimens increased as the weight gain decreased. The results are presented in Figure 1. The most substantial weight gain occurred within the initial 2–4 h of testing.

Among the specimens, those with 5 vol. %. of La_2O_3 exhibited the lowest weight gain after the 20-hour exposure. It is worth noting that up to 9 h of exposure, the differences in specific weight gain were minimal. Only with further increases in oxidation time did the impact

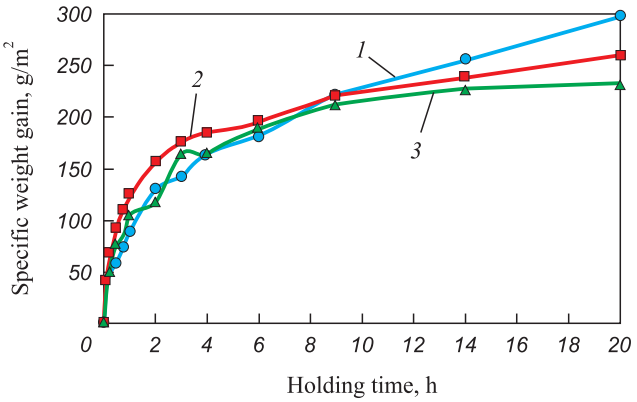

Fig. 1. Specific weight gain of ZrB_2–20 vol. % SiC ceramic specimens with different content of La_2O_3 after oxidation for 20 h at 1200 °C
La_2O_3, vol. %: ***1*** – 0, ***2*** – 2 and ***3*** – 5

Рис. 1. Удельный привес образцов керамики ZrB_2–20 об. % SiC с различным содержанием La_2O_3 после окисления в течение 20 ч при t = 1200 °C
La_2O_3, об. %: ***1*** – 0, ***2*** – 2 и ***3*** – 5

of La_2O_3 on the material's oxidation resistance become more pronounced.

It has been established that the resistance of ZrB_2 composite materials to high-temperature oxidation is primarily influenced by the composition of the protective layer formed on the material's surface [18]. The fractures in the specimens were examined using scanning electron microscopy (SEM) along with energy dispersive analysis. SEM images and maps displaying the distribution of silicon, zirconium, and boron within the specimens were obtained (Figure 2: spectrum *1* represents the surface layer of the specimen; spectrum *2* corresponds to an internal structure displaying significant visual dissimilarity; spectrum *3* pertains to a deeper layer of the material).

In the specimen without the addition of La_2O_3, a continuous protective layer composed of silicon-containing phases is formed on its surface (spectrum *1* in Fig. 2). When La_2O_3 is introduced, the silicon content on the specimen surface is also higher (spectrum *1*) compared to the subsequent layers (spectra 2 and *3*). However, the thickness of these layers is significantly reduced. Figure 3 presents a histogram depicting the calculated thickness of the oxidized layers, determined through analysis of the material's microstructure (as shown in Figure 2).

Table 1 displays the outcomes of the energy dispersive analysis, providing the elemental composition of the specimens following a 20-hour oxidation process. The first layer exhibits identical composition across all three cases. Notably, boron is not detected in the spectra, which is consistent with the challenges in accurately capturing elements from the second period of the periodic table using spectral methods [19].

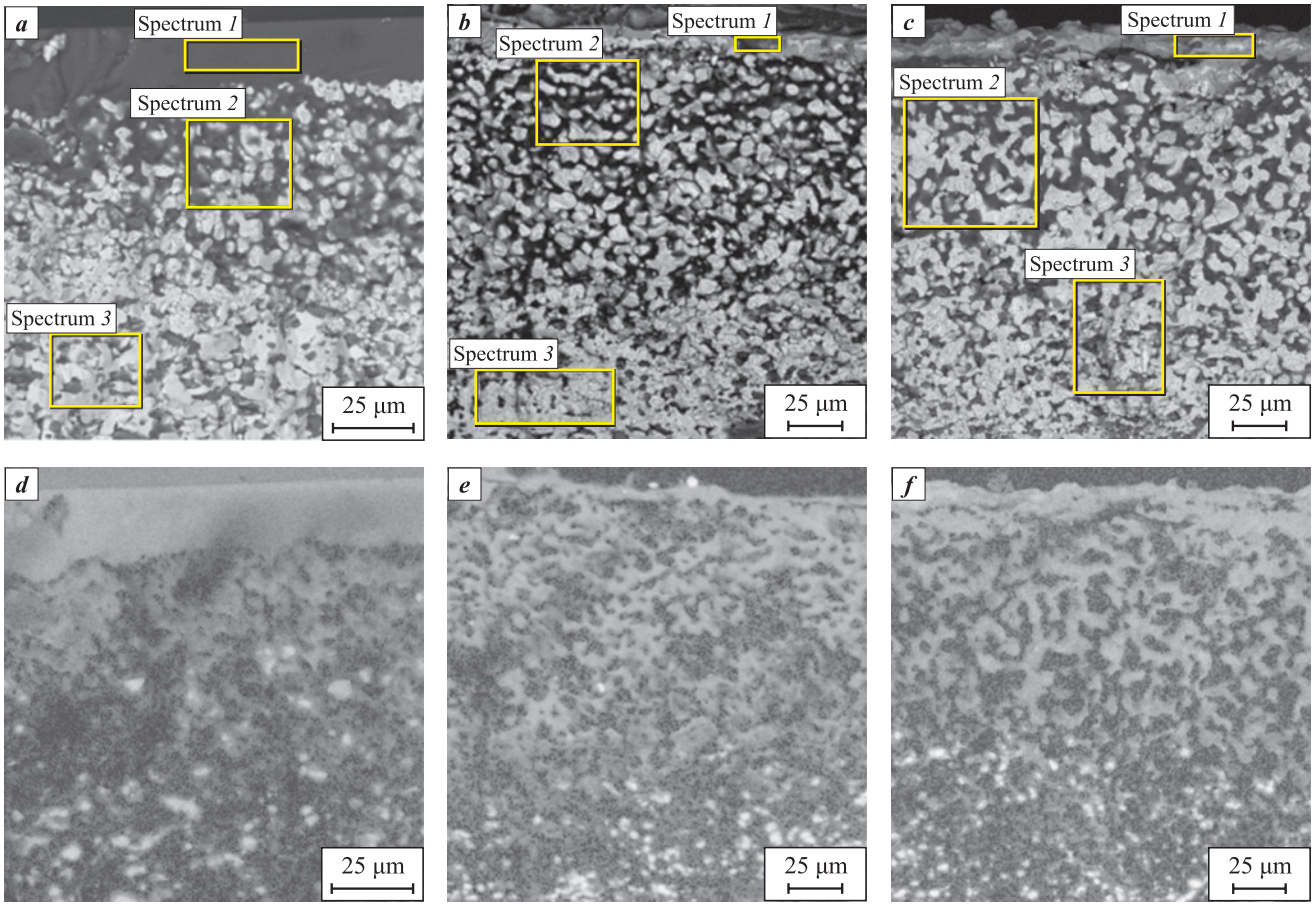

Fig. 2. SEM-images of fractures (***a–c***) and silicon distribution maps (***d–f***) after oxidation for 20 h of ZrB_2–20 vol. % SiC specimens
Addition of La_2O_3, vol. %: 0 (***a***, ***d***), 2 (***b***, ***e***) and 5 (***c***, ***f***)
White and light gray colors on distribution maps – silicon-containing phases

Рис. 2. СЭМ-изображения изломов (***a–c***) и карты распределения кремния (***d–f***) после окисления в течение 20 ч образцов состава ZrB_2–20 об. % SiC
Добавка La_2O_3, об. %: 0 (***a***, ***d***), 2 (***b***, ***e***) и 5 (***c***, ***f***)
Белый и светло-серый цвета на картах распределения – кремнийсодержащие фазы

Table 1. **Outcomes of the energy dispersive analysis of the elemental composition of the specimens after oxidation for 20 h**

Таблица 1. **Результаты энергодисперсионного анализа элементного состава образцов после окисления в течение 20 ч**

Imaging place (see Figure 2)	Elemental composition (wt. %) with the addition of La_2O_3, vol. %		
	0	2	5
Spectrum *1* Upper layer	O – 40.43 Si – 54.45 Zr – 2.90	O – 33.36 Si – 12.12 Zr – 54.52	O – 41.41 Si – 12.06 Zr – 46.53
Spectrum *2* Oxidized intermediate layer	O – 38.25 Si – 11.33 Zr – 47.81	O – 46.39 Si – 5.80 Zr – 36.77 B – 9.79 La – 0.55	O – 45.47 Si – 6.10 Zr – 46.96
Spectrum *3* Oxidized layer	O – 8.34 Si – 8.43 Zr – 48.42 B – 34.50	O – 24.96 Si – 3.45 Zr – 57.90 B – 13.13	O – 33.16 Si – 5.28 Zr – 53.60 B – 7.58

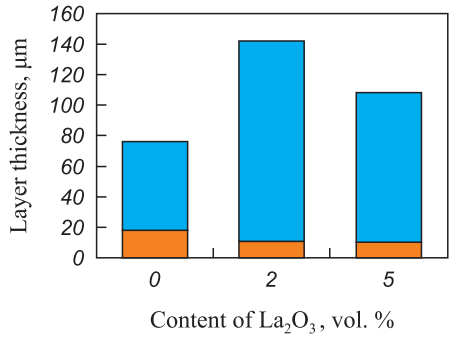

Fig. 3. Dependence of the thickness of oxidized layers on the surface of specimens of the ZrB_2–20 vol. % SiC composition without additives and with addition of 2 and 5 vol. % La_2O_3 after oxidation for 20 h
■ – spectrum *1*, ■ – spectrum *2* (see Fig. 2)
The third layer is not shown because it was only partially in the imaging area

Рис. 3. Зависимость толщины окисленных слоев на поверхности образцов состава ZrB_2–20 об. % SiC без добавки и с введением 2 и 5 об. % La_2O_3 после окисления в течение 20 ч
■ – спектр *1*, ■ – спектр *2* (см. рис. 2)
Третий слой не приведен, так как в зону съемки он попал лишь частично

Table 2 presents the results of calculating the atomic composition of the layers, with values rounded to the first decimal place after considering the atomic weights of the elements (and then multiplied by 10).

The assumed chemical composition is derived from the known composition of the initial specimens and the determined element ratios within the layers. The primary stoichiometric phases that are likely to be present are listed in Table 2. It should be noted that the formation of silicon monoxide as a crystalline compound has been previously documented in multiple instances [20–22].

The possibility of non-stoichiometric compound formation, such as borosilicate and borate glasses, should also be taken into consideration [23].

Raman spectroscopy confirmed the presence of zircon ($ZrSiO_4$) and monoclinic zirconium dioxide (ZrO_2) as the main phases of the oxidized material (Figure 4) [24]. The imaging was conducted from the surface of the specimens, thereby removing the first layer. One of the obtained spectra is presented, with the others being identical. The only distinction lies in the intensity ratio of the peaks corresponding to the main phases. The absence of silicon oxide lines in the specimen without lanthanum addition can be explained by the fact that well-oxidized phases in the second layer hinder the detection of amorphous or concealed-crystalline silicon oxide phases.

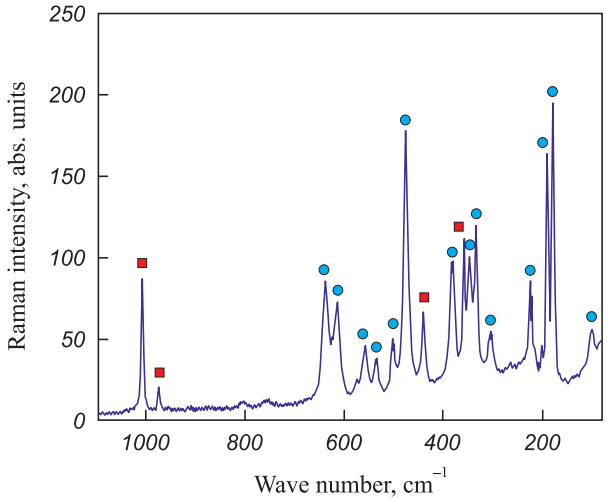

Fig. 4. Fragment of the Raman spectrum of the upper oxidized layer on the surface of a specimen with addition of 5 vol. % La_2O_3 after oxidation for 20 h
Designations of crystalline phases:
■ – zircon; ● – monoclinic zirconium dioxide

Рис. 4. Фрагмент КР-спектра верхнего окисленного слоя на поверхности образца состава с добавкой 5 об. % La_2O_3 после окисления в течение 20 ч
Обозначения кристаллических фаз:
■ – циркон; ● – моноклинный диоксид циркония

Table 2. **Ratio of elements in the layers after oxidation**

Таблица 2. **Соотношение элементов в слоях после окисления**

Imaging place (see Figure 2)	Ratio of elements and the most probable chemical composition with the La_2O_3 content, vol. %		
	0	2	5
Spectrum *1* Upper layer	**$Zr_{0,3}Si_{19}O_{25}$** SiO_2 and SiO	**$Zr_6Si_4O_{21}$** $ZrSiO_4$ and ZrO_2 Insignificant oxygen excess	**$Zr_5Si_4O_{26}$** $ZrSiO_4$ and ZrO_2 Oxygen excess
Spectrum *2* Oxidized intermediate layer	**$Zr_5Si_4O_{24}$** $ZrSiO_4$ and ZrO_2 Oxygen excess	**$Zr_4Si_2O_{29}B_9$** ZrB_2, $ZrSiO_4$ Oxygen excess	**$Zr_5Si_2O_{28}$** $ZrSiO_4$ and ZrO_2 Oxygen excess
Spectrum *3* Oxidized layer	**$Zr_5Si_3O_5B_{32}$** ZrB_2, SiO_2 or SiO Significant boron excess	**$Zr_6SiO_{16}B_{12}$** ZrB_2, SiO_2 Oxygen excess	**$Zr_6Si_2O_{21}B_7$** ZrB_2, $ZrSiO_4$ Oxygen excess

There is a noticeable disparity in the distribution of zirconium on the surface of specimens with and without La_2O_3 (Figure 5, *a*–*c*). In the case without La_2O_3, ZrO_2, despite its relatively low overall content (as seen in Table 1), is distributed relatively (Figure 5, *a*). Presumably, it is integrated within the primary silicon-containing phases. However, the addition of lanthanum oxide results in the growth of zirconium-bearing phase grains and the emergence of agglomerates and large pores between these phases. In this scenario, the formation of silicon oxides is unlikely.

Figure 5, *d* illustrates a fragment of the boron distribution map in the upper layer of the specimen containing 5 vol. % La_2O_3, corresponding to the fragment of the zirconium distribution map in Figure 5, *c*. Since boron could not be detected during the determination of the mass content of elements (as indicated in Table 1), it can be inferred that boron is present in the form of silicate glasses (refer to Figure 2, *f*) that fill the gaps between zircon and zirconium dioxide grains [25].

Consequently, on the surface of specimens without La_2O_3 additives, phases comprising silicon oxides with traces of boron and zirconium oxides are formed. In the presence of La_2O_3 additives, the main phases observed are zirconium dioxide and zircon, along with an excess of oxygen. However, neither case effectively acts as a significant barrier against the deep penetration of oxygen into the material. The presence of lanthanum oxide appears to enhance the formation of zircon, a phase that exhibits greater resistance to thermal shock than monoclinic zirconium dioxide and contributes to the deceleration of the oxidation process.

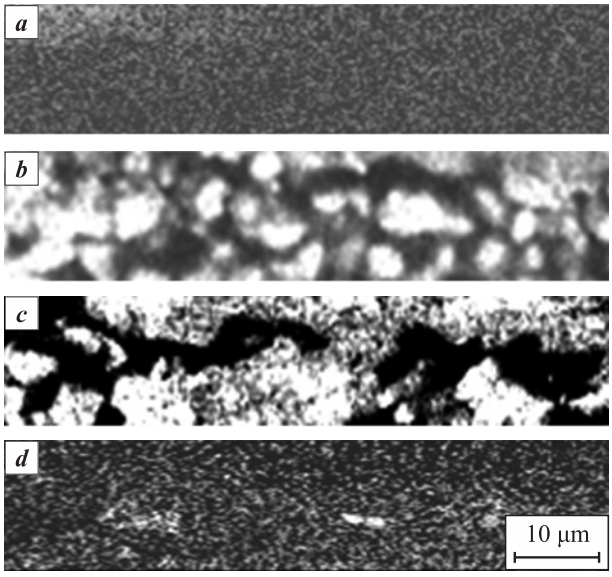

Fig. 5. Fragments of distribution maps of zirconium (***a***–***c***) and boron (***d***)

Рис. 5. Фрагменты карт распределения циркония (***a***–***c***) и бора (***d***)

Conclusion

The aim of the study was to investigate the impact of La_2O_3 addition on the oxidation properties of composite ceramics with a composition of 80 vol. % ZrB_2 and 20 vol. % SiC, consolidated through spark plasma sintering. The materials were examined in three variations: without La_2O_3, with 2 vol. % La_2O_3 and 5 vol. % La_2O_3. In all cases, SiC acted as a sacrificial material, being the first to undergo oxidation. Specimens without La_2O_3 addition exhibited a surface layer consisting mainly of SiO_2 and SiO. On the other hand, specimens with La_2O_3 addition showcased surface layers composed primarily of $ZrSiO_4$ and ZrO_2.

Consequently, the introduction of La_2O_3 intensified the formation of zircon and decelerated the oxidation processes. However, it did not serve as a complete barrier to the deep penetration of oxygen into the material.

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Information about the Authors

Valentina B. Kulmetyeva – Cand. Sci. (Eng.), Associate Professor, Department of Mechanics of Composite Materials and Structures, Perm National Research Polytechnic University (PNRPU).
ORCID: 0000-0002-5214-0932
E-mail: kulmetevavb@pstu.ru

Vyacheslav E. Chuvashov – PhD student, Department of Mechanics of Composite Materials and Structures, PNRPU.
ORCID: 0009-0000-0171-2024
E-mail: slavachuvashov@yandex.ru

Kseniya N. Lebedeva – Master's Student, Department of Mechanics of Composite Materials and Structures, PNRPU.
ORCID: 0009-0003-6134-2952
E-mail: lebedkseni@mail.ru

Svetlana E. Porozova – Dr. Sci. (Eng.), Professor, Department of Mechanics of Composite Materials and Structures, PNRPU.
ORCID: 0000-0001-5835-9727
E-mail: sw.porozova@yandex.ru

Maksim N. Kachenyuk – Dr. Sci. (Eng.), Associate Professor, Department of Mechanics of Composite Materials and Structures, PNRPU.
ORCID: 0000-0001-7476-9734
E-mail: maxxkach@yandex.ru

Сведения об авторах

Валентина Борисовна Кульметьева – к.т.н., доцент кафедры механики композиционных материалов и конструкций (МКМК), Пермский национальный исследовательский политехнический университет (ПНИПУ).
ORCID: 0000-0002-5214-0932
E-mail: kulmetevavb@pstu.ru

Вячеслав Эдуардович Чувашов – аспирант кафедры МКМК, ПНИПУ.
ORCID: 0009-0000-0171-2024
E-mail: slavachuvashov@yandex.ru

Ксения Николаевна Лебедева – магистрант кафедры МКМК, ПНИПУ.
ORCID: 0009-0003-6134-2952
E-mail: lebedkseni@mail.ru

Светлана Евгеньевна Порозова – д.т.н., профессор кафедры МКМК, ПНИПУ.
ORCID: 0000-0001-5835-9727
E-mail: sw.porozova@yandex.ru

Максим Николаевич Каченюк – д.т.н., доцент кафедры МКМК, ПНИПУ
ORCID: 0000-0001-7476-9734
E-mail: maxxkach@yandex.ru

Contribution of the Authors

V. B. Kulmetyeva – conceptualization, goal setting, research objectives formulation, and thermal cycling of specimens.

V. E. Chuvashov – preparation of charge for spark plasma sintering, conducting high-temperature oxidation, data analysis, experimental results interpretation, of research result processing.

K. N. Lebedeva – analysis of experimental results, research results processing, article writing.

S. E. Porozova – scientific supervision, research results processing, text preparation and editing.
M. N. Kachenyuk – conducting spark plasma sintering.

Вклад авторов

В. Б. Кульметьева – постановка цели и задач исследования, формирование основной концепции, проведение термоциклирования образцов.
В. Э. Чувашов – подготовка шихты для проведения искрового плазменного спекания, подготовка и проведение высокотемпературного окисления, проведение расчетов, анализ полученных результатов экспериментов, обработка результатов исследований.
К. Н. Лебедева – анализ полученных результатов экспериментов, обработка результатов исследований, подготовка текста статьи.
С. Е. Порозова – научное руководство, обработка результатов исследований, подготовка и корректировка текста статьи.
М. Н. Каченюк – проведение искрового плазменного спекания.

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