EXTENDED ABSTRACT

Scope of the Dissertation

The scope of the dissertation is focused on the investigation of hot corrosion behaviour of advanced ceramic thermal barrier coatings exposed to molten sulfate and sulfate–vanadate salt environments at elevated temperatures. The research addresses a critical limitation of conventional yttria-stabilised zirconia thermal barrier coatings, namely their chemical instability and accelerated degradation in the presence of molten deposits originating from fuel impurities, airborne contaminants, and corrosive species present in industrial and aviation gas turbines. The dissertation covers the development, deposition, and systematic evaluation of single-phase and composite ceramic topcoats based on neodymium zirconate ($Nd_2Zr_2O_7$) and neodymium cerate ($Nd_2Ce_2O_7$), combined with 8 wt.% yttria-stabilised zirconia (8YSZ). The coatings were designed to operate under realistic service conditions, where molten sodium sulfate (Na_2SO_4), sodium sulfate–magnesium sulfate (Na_2SO_4–$MgSO_4$), and sodium sulfate–vanadium pentoxide (Na_2SO_4–V_2O_5) mixtures form aggressive corrosive melts on component surfaces.

A particular and original aspect of the dissertation is the detailed investigation of hot corrosion phenomena in Na_2SO_4–$MgSO_4$ environments. Although sodium sulfate-induced hot corrosion has been widely reported in the literature, the combined effect of sodium and magnesium sulfates, which form low-melting eutectics with enhanced penetrability and chemical reactivity, remains poorly understood. The dissertation therefore fills an important research gap by systematically analysing the degradation mechanisms of rare-earth-based thermal barrier coatings in Na_2SO_4–$MgSO_4$ molten salts.

Dissertation Objectives:

Based on literature research that highlights gaps in knowledge regarding thermal barrier coatings, particularly two-phase composite coatings of the $Ln_2Zr_2O_7$ + 8YSZ or $Ln_2Ce_2O_7$ + 8YSZ type, especially their corrosion resistance in liquid sulfate salt deposits with and without vanadium oxide, the following thesis was proposed for this doctoral dissertation.

Thermal barrier coatings with a composite two-phase ceramic insulating layer of $Nd_2Zr_2O_7$ + 8YSZ and $Nd_2Ce_2O_7$ + 8YSZ are expected to exhibit higher durability under hot corrosion test conditions compared to traditional single-phase TBC systems. This is due to the increased stress compensation capacity and, consequently, better deformation tolerance (fracture toughness) of two-phase systems. This phenomenon is related to previously unidentified degradation mechanisms in two-phase systems, involving interactions between the pyrochlore/fluorite phase and 8YSZ, which lead to the formation of non-stoichiometric phases and numerous ultrafine voids. These voids help to compensate for the nucleation and growth of microcracks. As a result, it will be possible to develop TBC systems resistant to macroscopic cracking and spallation of the ceramic layer. The intensity of decomposition of the initial phases, $Nd_2Zr_2O_7$ and $Nd_2Ce_2O_7$, will depend on the compositions of the sulphate salts used in the study, especially their tendency to form low-melting eutectics that speed up the decomposition process.

To demonstrate this, the following studies will be undertaken:

- Evaluation of the high-temperature corrosion resistance of $Nd_2Zr_2O_7$-type TBC systems and the composite systems: $Nd_2Zr_2O_7$ + 8YSZ and $Nd_2Ce_2O_7$ + 8YSZ in an environment of liquid Na_2SO_4 salt deposits, a Na_2SO_4 + $MgSO_4$ salt mixture, and Na_2SO_4 salt with added V_2O_5;

- Studies of the phase composition of the TBC systems at individual stages of corrosion resistance testing.

- Studies of the surface layer condition of the analysed systems and their cross-sectional sections.

These studies are aimed at achieving specific objectives:

- Determining the factors determining the durability of the TBC systems under the test conditions

- Determining the microstructural and phase composition changes in the tested TBC systems induced by temperature and environmental factors.

- Determining the microstructural mechanisms influencing the degradation process of the tested TBC systems.

- Identification of mechanisms determining the course of corrosion processes and their reference to generally available knowledge in the field of high-temperature corrosion processes of TBC systems based on rare-earth zirconates and cerates.

Description of the Research Subject:

Thermal barrier coatings are multilayer protective systems designed to thermally insulate metallic components operating at high temperatures. In the present research, the coatings consisted of an Inconel 625 nickel-based superalloy substrate, a NiCrAlY metallic bond coat, a thermally grown oxide layer, and a ceramic topcoat. The ceramic topcoats were deposited using atmospheric plasma spraying and consisted of either single-phase $Nd_2Zr_2O_7$ or dual-phase composite systems incorporating 8YSZ.

Neodymium zirconate was selected as a representative pyrochlore-structured rare-earth zirconate due to its low thermal conductivity and high-temperature phase stability. Neodymium cerate, exhibiting a defect-fluorite crystal structure, was investigated as an alternative material with potentially superior resistance to vanadium-induced chemical degradation. Composite coatings were designed to combine the advantageous thermal properties of rare-earth oxides with the established mechanical reliability and strain tolerance of yttria-stabilised zirconia.

Materials and Methods:

The coatings were deposited using atmospheric plasma spraying under controlled parameters. The chemical composition of the Inconel 625 substrate is presented in Table 1.1.

Table 1.1: Chemical composition of the IN 625 substrate alloy

Wt%	Ni	Cr	Fe	Mo	Co	Nb	Al	Mn	Si	Ti	P	C	S
In 625	60.7	21.67	4.27	8.96	0.07	3.56	0.14	0.07	0.08	0.18	0.007	0.01	0.0003

The spraying parameters are summarized in Table 1.2.

Table 1.2: TBCs coating spraying process parameters.

Parameters	**Powder type**		
	8YSZ	$Nd_2Zr_2O_7$	$Nd_2Ce_2O_7$
Burner type	F4MB	F4MB	F4MB
argon [l/min]	40	40	40
hydrogen [l/min]	10	10	10
Powder carrier	2,6	2,6	2,6
Powder feeding	15	15	15
Current [A]	600	600	600
Arc voltage [V]	61,6-62,3	61,6-62,3	61,6-62,3
Burner power [kW]	37,2-38,1	37,2-38,1	37,2-38,1
Mixing	60	60	60
Rotation [RPM]	120	120	120
Instrument diameter	150	150	150
Feed [mm/s]	10	10	10
Distance[mm]	100	100	100
Number of program cycles	8	8	8

Hot corrosion tests were conducted at 920 °C using three corrosive environments, with test parameters listed in Table 1.3. Phase composition was analysed by X-ray diffraction, while microstructural and chemical changes were examined using scanning electron microscopy and energy-dispersive spectroscopy.

Table 1.3: Hot corrosion test parameters and conditions

Thermal Barrier Coating Systems	Corrosion Environment	Time of Exposer	Temperature
$Nd_2Zr_2O_7$	Na_2SO_4	120 h	920 °C
	$Na_2SO_4 + MgSO_4$ (50/50)	120 h	920 °C
	$Na_2SO_4 + V_2O_5$ (50/50)	36 h	920 °C
$Nd_2Zr_2O_7$ + 8YSZ (50/50)	Na_2SO_4	224 hours	920 °C
	$Na_2SO_4 + MgSO_4$ (50/50)	224 hours	920 °C
	$Na_2SO_4 + V_2O_5$ (50/50)	64 hours	920 °C
	Na_2SO_4	168 h	920 °C

$Nd_2Ce_2O_7$ + 8YSZ (50/50)	Na_2SO_4 + $MgSO_4$ (50/50)	168 h	920 °C
	Na_2SO_4 + V_2O_5 (50/50)	48 h	920 °C

Main Results:

Plasma-sprayed NZO coatings demonstrated different hot corrosion behaviour depending on the type of molten salt environment. In the presence of Na_2SO_4, the coatings retained partial phase stability; however, the formation of monoclinic ZrO_2 and sodium oxides indicated the early stages of degradation. Exposure to a Na_2SO_4–$MgSO_4$ mixture led to the formation of a eutectic phase at approximately 660 °C, which accelerated microstructural damage, including grain boundary attack, microcracking, and the development of $Nd_2(SO_4)_3$ and MgO. The most severe degradation occurred in the Na_2SO_4–V_2O_5 environment, where rapid pyrochlore decomposition resulted in the formation of $NdVO_4$ and monoclinic zirconia, causing extensive cracking and premature coating failure. Overall, the findings indicate that NZO coatings provide moderate resistance to sulfate-based salts but are highly susceptible to vanadate-induced corrosion. To improve long-term durability, future approaches should consider multilayer coating architectures or compositional modifications designed to reduce vanadate reactivity while preserving the high-temperature stability of NZO.

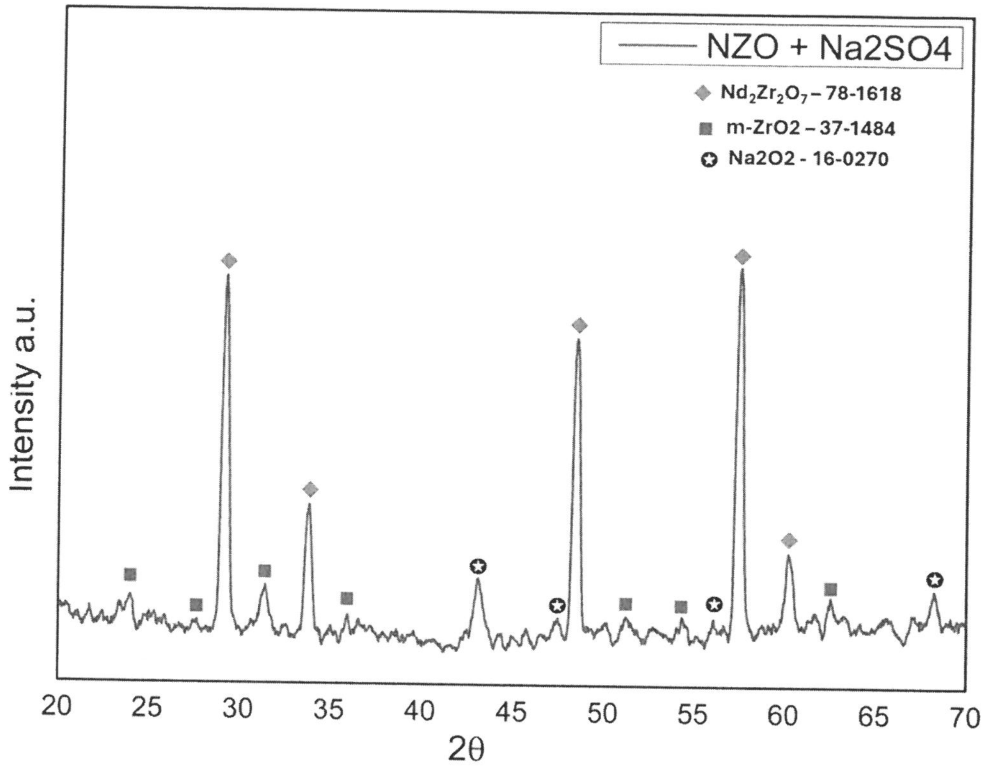


Figure 1.1: XRD Pattern of $Nd_2Zr_2O_7$ TBCs after 120 h Exposure in Pure Na_2SO_4 Environment

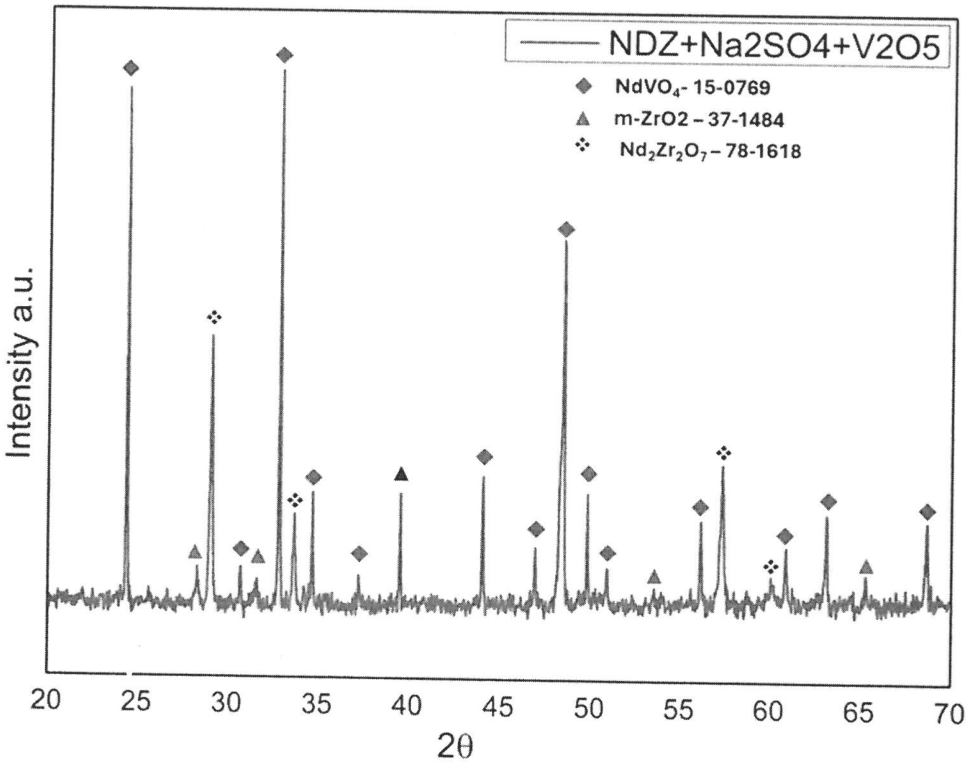
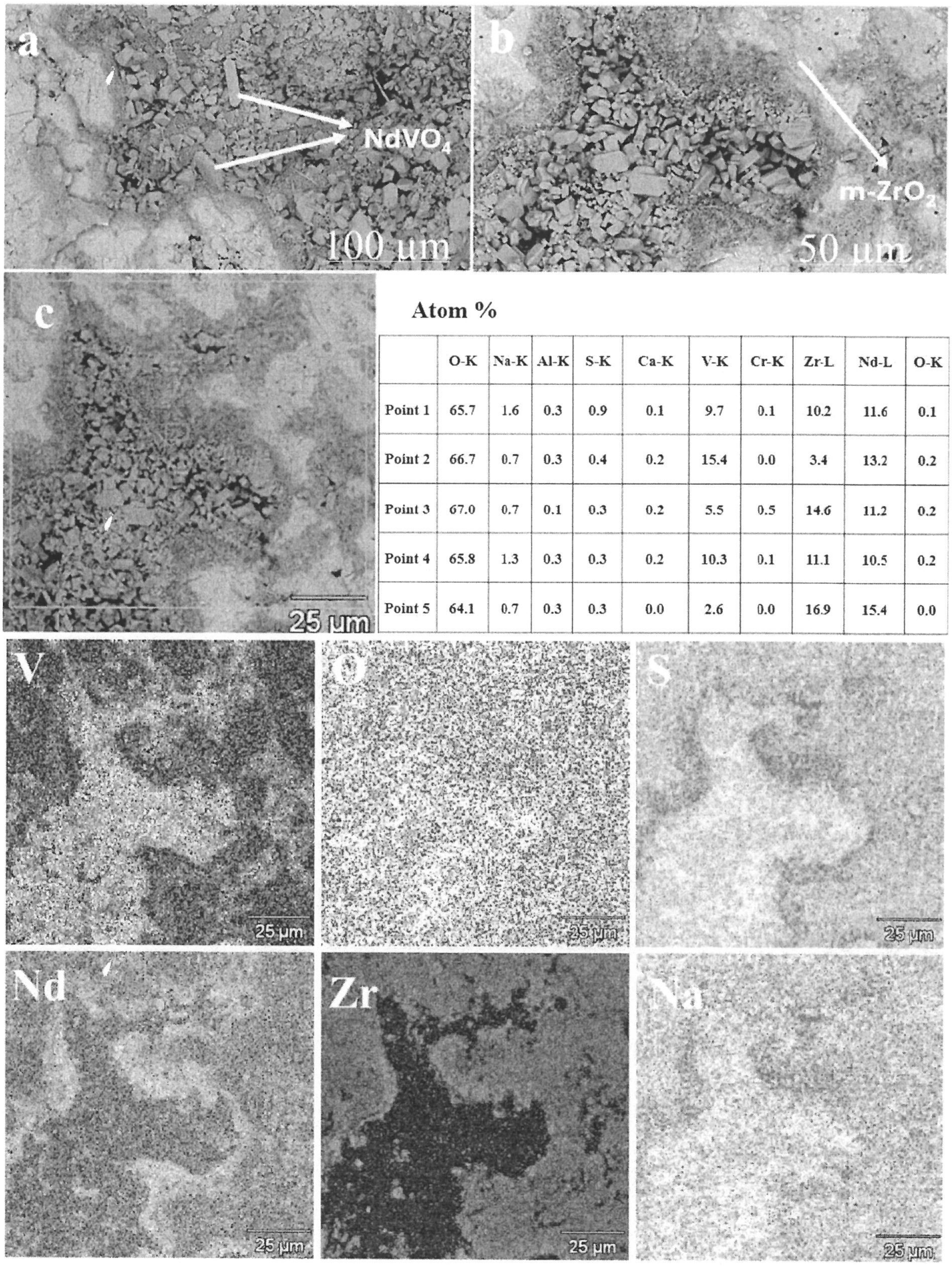


Figure 1.2: XRD Pattern of $Nd_2Zr_2O_7$ TBCs after 36 h Exposure in Na_2SO_4-V_2O_5 Environment.



Atom %

	O-K	Na-K	Al-K	S-K	Ca-K	V-K	Cr-K	Zr-L	Nd-L	O-K
Point 1	65.7	1.6	0.3	0.9	0.1	9.7	0.1	10.2	11.6	0.1
Point 2	66.7	0.7	0.3	0.4	0.2	15.4	0.0	3.4	13.2	0.2
Point 3	67.0	0.7	0.1	0.3	0.2	5.5	0.5	14.6	11.2	0.2
Point 4	65.8	1.3	0.3	0.3	0.2	10.3	0.1	11.1	10.5	0.2
Point 5	64.1	0.7	0.3	0.3	0.0	2.6	0.0	16.9	15.4	0.0

Figure 1.3: SEM and EDS Analysis of NZO Coatings after 36 h Hot Corrosion in Na_2SO_4-V_2O_5 Environment.

Microstructural studies conducted on the TBC coating system type 50 $Nd_2Zr_2O_7$ + 50 8YSZ under the conditions of sulphate salts in the presence of vanadium oxide revealed several significant degradation phenomena. In the as-sprayed condition, the pyrochlore phase of $Nd_2Zr_2O_7$ was partially decomposed into non-stoichiometric compounds with a fluorite-type network. This phenomenon resulted from doping the pyrochlore phase with Y_2O_3 derived from 8YSZ, which led to a condition in which the more stable phase was a zirconate compound with a fluorite-type lattice. Under hot-corrosion test conditions, the decomposition process of the pyrochlore phase was intensified; however, the overall intensity of degradation remained moderate. A significant effect of degradation was the formation of numerous ultrafine voids in the zirconate phase, a phenomenon also confirmed in other binary systems such as $Gd_2Zr_2O_7$ + 8YSZ and $Sm_2Zr_2O_7$ + 8YSZ.

The degradation processes of the $Nd_2Zr_2O_7$ + 8YSZ system were significantly more intense in an environment containing a mixture of sodium and magnesium sulphate salts. Due to the lowered melting temperature of this mixture compared to pure sodium sulphate salt, a much greater penetration of corrosive atmospheric components into the ceramic layer was observed. Furthermore, analysis of the system in an environment containing Na_2SO_4 salt and vanadium oxide demonstrated complete decomposition of neodymium zirconate, resulting in the formation of neodymium vanadate, as well as partial decomposition of the 8YSZ phase, which led to the formation of yttrium vanadate and monoclinic zirconium oxide.

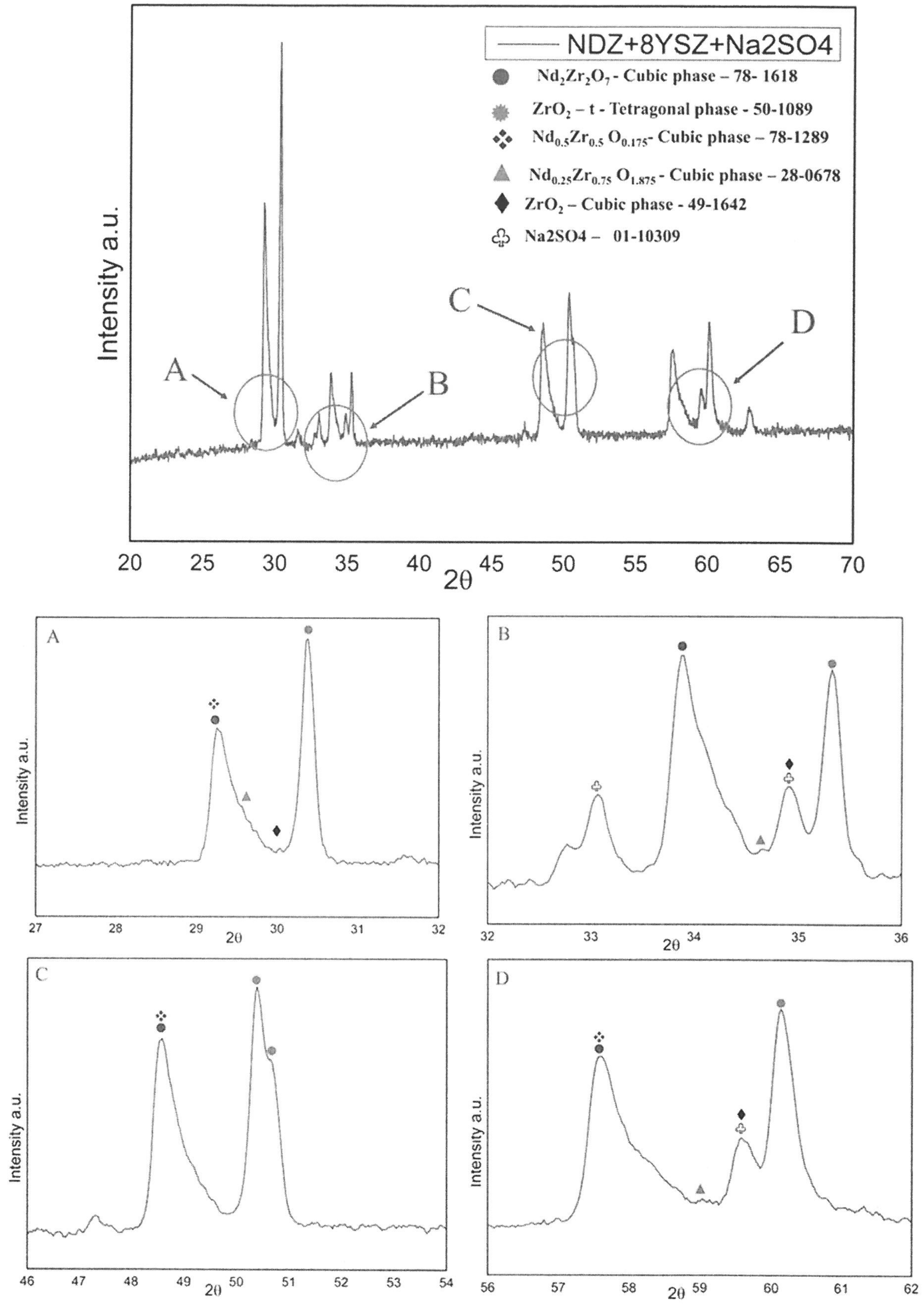
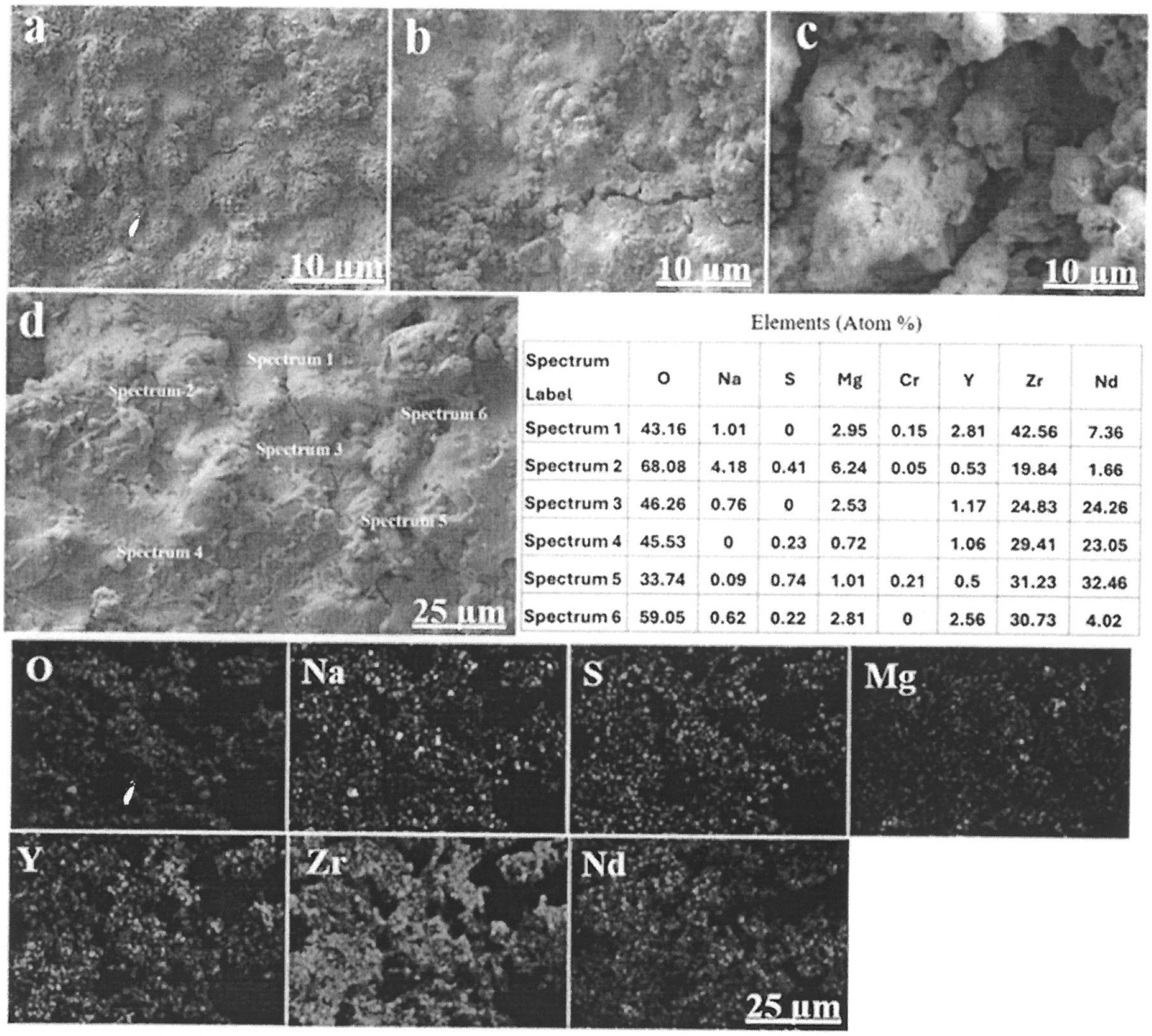


Figure 1.4: XRD pattern of 50 $Nd_2Zr_2O_7$ + 50 8YSZ after hot corrosion at 920 °C in liquid Na_2SO_4 salt.



Elements (Atom %)

Spectrum Label	O	Na	S	Mg	Cr	Y	Zr	Nd
Spectrum 1	43.16	1.01	0	2.95	0.15	2.81	42.56	7.36
Spectrum 2	68.08	4.18	0.41	6.24	0.05	0.53	19.84	1.66
Spectrum 3	46.26	0.76	0	2.53		1.17	24.83	24.26
Spectrum 4	45.53	0	0.23	0.72		1.06	29.41	23.05
Spectrum 5	33.74	0.09	0.74	1.01	0.21	0.5	31.23	32.46
Spectrum 6	59.05	0.62	0.22	2.81	0	2.56	30.73	4.02

Figure 1.5: Surface morphology and chemical composition of 50 $Nd_2Zr_2O_7$ + 50 8YSZ TBC systems after hot corrosion at 920 °C for 224 hours in a Na_2SO_4 + $MgSO_4$ salt mixture.

Microstructural studies characterising the behaviour of the 50 $Nd_2Ce_2O_7$ + 50 8YSZ TBC coating system under sulphate salts in the presence of vanadium oxide showed that the composite thermal barrier coating retained a stable dual-phase structure composed of cubic fluorite $Nd_2Ce_2O_7$ and cubic YSZ, demonstrating good phase compatibility after high-temperature exposure. In a pure Na_2SO_4 environment, the coating exhibited relatively mild degradation, with limited formation of $Nd_2O_2SO_4$ and minor monoclinic ZrO_2, indicating good resistance to sulphate attack. In contrast, exposure to a Na_2SO_4–$MgSO_4$ molten salt environment resulted in more pronounced surface reactions, extensive formation of reaction products, and increased sulphur penetration, showing that the addition of $MgSO_4$ intensified chemical interactions and enhanced molten salt corrosion rather than suppressing it. The most severe degradation occurred in the Na_2SO_4–V_2O_5 environment, where the formation of $NdVO_4$

and monoclinic ZrO_2, together with extensive surface damage and increased porosity, reflected aggressive vanadate attack. SEM–EDS analysis confirmed that corrosion reactions predominantly affected the Na_2SO_4 phase, whereas the YSZ phase exhibited comparatively higher chemical stability and contributed to partial retention of coating integrity. Despite these degradation processes, the coating–substrate interface remained well bonded under all corrosion conditions, with only a thin thermally grown oxide (TGO) layer observed, indicating good adhesion and thermal compatibility of the multilayer system.

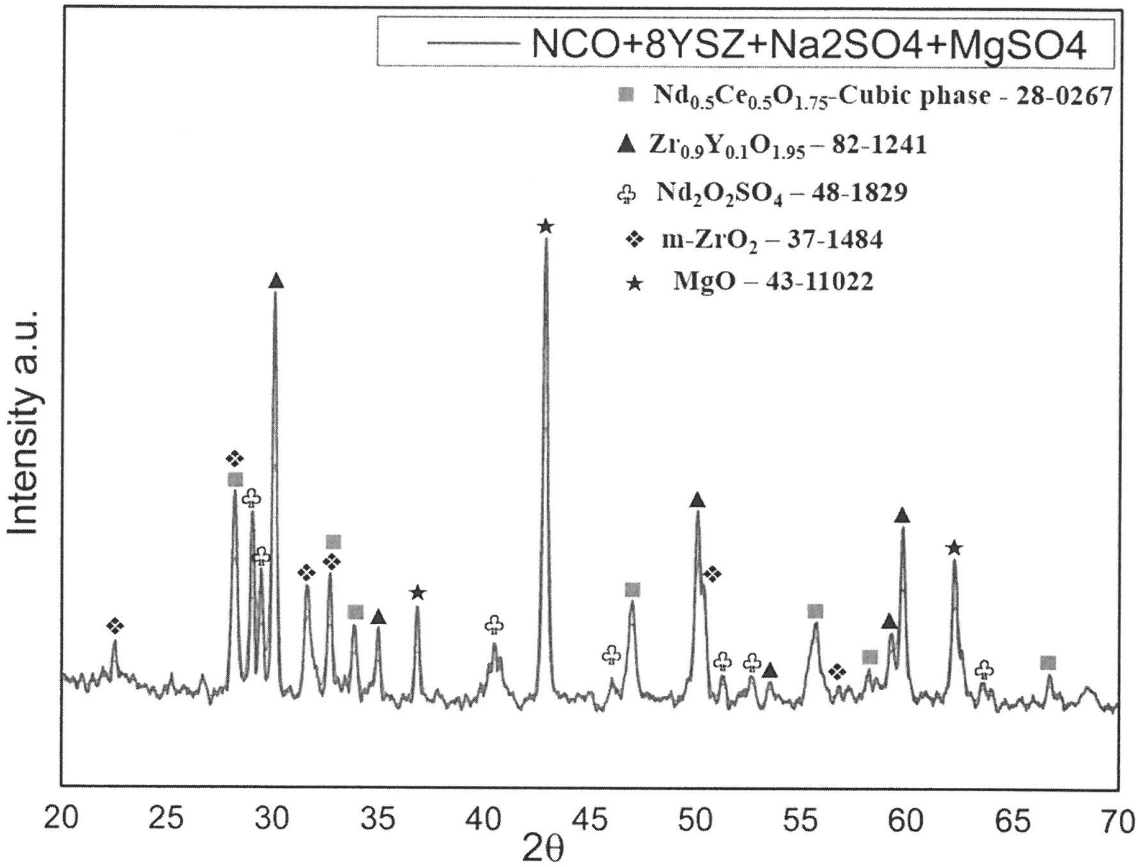
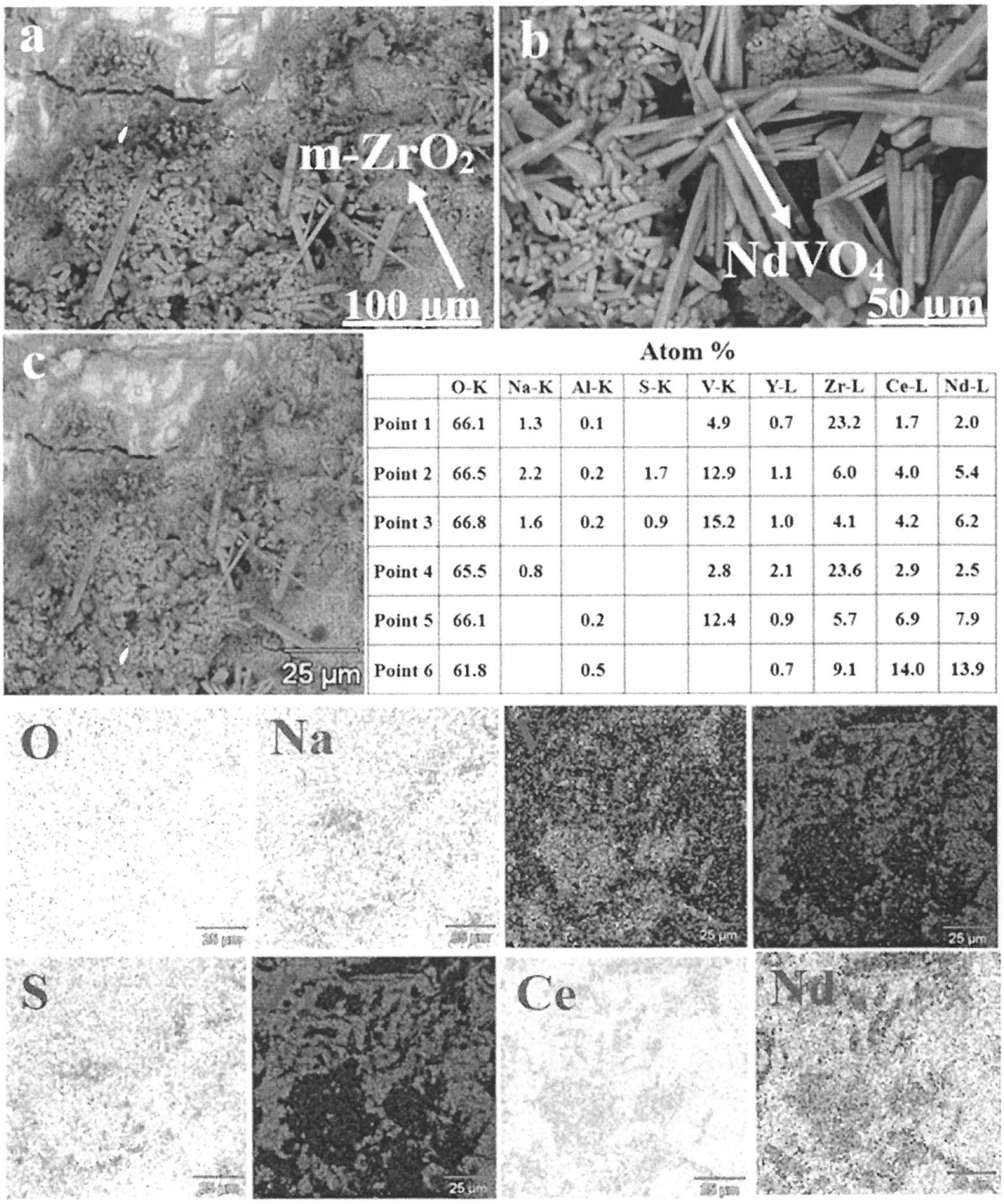


Figure 1.6: XRD pattern of the $Nd_2Ce_2O_7$+ 8YSZ coating after hot corrosion in an equimolar Na_2SO_4–$MgSO_4$ mixture at 920 °C for 168 h.



Atom %

	O-K	Na-K	Al-K	S-K	V-K	Y-L	Zr-L	Ce-L	Nd-L
Point 1	66.1	1.3	0.1		4.9	0.7	23.2	1.7	2.0
Point 2	66.5	2.2	0.2	1.7	12.9	1.1	6.0	4.0	5.4
Point 3	66.8	1.6	0.2	0.9	15.2	1.0	4.1	4.2	6.2
Point 4	65.5	0.8			2.8	2.1	23.6	2.9	2.5
Point 5	66.1		0.2		12.4	0.9	5.7	6.9	7.9
Point 6	61.8		0.5			0.7	9.1	14.0	13.9

Figure 1.7: SEM and EDS analysis of the $Nd_2Ce_2O_7$+ 8YSZ coating after hot corrosion in an equimolar Na_2SO_4–V_2O_5 mixture at 920 °C for 48 h.

Conclusion:

Single-phase thermal barrier coating systems based on neodymium zirconate demonstrate excellent resistance to the corrosive effects of environments containing liquid sulfate salt deposits, both Na_2SO_4 and $Na_2SO_4/MgSO_4$ mixtures.

The primary degradation mechanism of $Nd_2Zr_2O_7$ TBC coatings is related to their high susceptibility to temperature and environmentally induced microcracks, as well as aggressive corrosive environments. The presence of microcracks and a high Young's modulus favours the generation of unfavorable stress states, resulting in ceramic layer spallation.

This indicates the need to increase the deformation tolerance (fracture toughness) of the ceramic layer, which should ensure increased operational durability in aggressive sulfate salt environments. The two-phase composite coatings of the $Nd_2Zr_2O_7$ + 8YSZ and $Nd_2Ce_2O_7$ + 8YSZ types demonstrated not only very favorable behaviour under the influence of liquid sulfate salts and their mixtures, but also maintained the overall integrity of the coating despite the formation of voids and microcracks in the ceramic layer's microstructure. This is due to the increased tolerance to deformation of the two-phase microstructure of the TBC coating.

Corrosion degradation processes in the tested TBC systems were associated with the interaction of liquid sulfate salts with neodymium zirconate or cerate, and the formation of neodymium sulfates or oxysulphates as primary corrosion products (to a limited extent).

The dominating second identified mechanism was the decomposition of neodymium zirconate with a pyrochlore lattice into non-stoichiometric zirconates with a fluorite lattice. In the case of neodymium cerate, the formation of non-stoichiometric compounds was observed only during corrosion in a mixture of liquid sodium and magnesium sulfate salts. The generation of numerous voids within the zirconate and cerate phases accompanies these processes.

Studies also showed that the mixture of Na_2SO_4 and $MgSO_4$ sulfate salts exhibited significantly higher levels of corrosion aggressiveness, resulting from the formation of a eutectic with a substantially lower melting point than the individual sulfates. This also reduces the viscosity of the liquid salt deposits, which intensifies the process of penetration into the porous structure of the TBC ceramic layer.

The introduction of V_2O_5 oxide into the corrosive environment rapidly accelerates the corrosion process of the tested TBC systems, regardless of their variant. This is due to the strong tendency to form neodymium vanadate, as well as yttrium vanadates, in the case of two-phase composite coatings.

References to the Author's Main Publications:

The results of this dissertation have been published in the following peer-reviewed journals:

1. **Khan, M. J.**, Moskal, G., Pakseresht, A., Parchoviansky, M., & Pęcak, K. (2025). Complex sulphate vanadate salt induced hot corrosion and thermal shock performance of $Nd_2Zr_2O_7$ + 8YSZ composite thermal barrier coating system. *Ceramics International, 51*(24B), 42551–42564. https://doi.org/10.1016/j.ceramint.2025.07.001
2. **Khan Muhammad Jahangir**, Moskal Grzegorz, Iqbal Amjad *[et al.]*, Coatings, 2023, vol. 13, no. 8, pp.1-14, Article number:1311. Go to the document by digital IDDOI:10.3390/coatings13081311.

Summary of the Author's Own Contribution:

As the First and Corresponding Author, Muhammad Jahangir Khan was principally responsible for the conceptual development of the study, formulation of the research methodology, and implementation of computational and analytical procedures. The author conducted the investigation, performed advanced formal analyses, curated the datasets, and authored the original manuscript. The author also led the manuscript revision and editorial process to ensure scientific rigor and coherence.