Corrosion Management ISSN: 1355-5243
(https://corrosion-management.com/)
Volume 35, Issue 02 – 2025
SCOPUS

NANO-ZIRCONIA COMPOSITE COATINGS AS EFFECTIVE BARRIERS FOR CORROSION MITIGATION

[1]*Rupambika Mohanty, [2]Sunita Routray, [1]Ranjita Swain and [1] Rudra Narayan Mohapatro

[1]Chemical Engineering Department,
[1]C. V. Raman Global University, Bhubaneswar, Odisha, India-752054.

[2]Mechanical Engineering Department,
[2] Centurion University of Technology and Management, Bhubaneswar, Odisha, India- 752050.
**Corresponding Author*

ABSTRACT

This work examines the corrosion resistance of nano zircon or zirconia-silica (ZrO_2-SiO_2) composite coatings on metal surfaces opened to corrosive ambient, comprised of acids, salts, and moisture. Looking at the traditional coatings, nano-scale composites upgrade reliability via augmenting hardness, wear resistance, and adhesion aspects. The synthesized zircon, provide greater cleanliness and steadiness over natural zircon, bring forth remarkable benefits toward industrial usages like aerospace and automotive sectors, diminishing maintenance costs and expanding service span. The ZrO_2-SiO_2 composite was artificially produced by extracting nano ZrO_2 out of zircon concentrate and mixing it with fumed SiO_2 in a 1:1 molar ratio, subsequently calcination at temperatures ranging 1000°C to 1400°C. X-ray diffraction (XRD) study established the configuration of monoclinic ZrO_2 and tetragonal $ZrSiO_4$, with finest crystallinity at 1400°C. Scanning Electron Microscopy (SEM) exposed a dense, regular, and crack-free coating with tough adhesion. The corrosion rate of mild steel coated with ZrO_2-SiO_2 composite is 0.001mm/year in sea water and .004mm/yr in 0.1M H_2SO_4solution. The results emphasize the prospective of ZrO_2-SiO_2 coatings as a useful resolution for corrosion defence in considerate manufacturing atmospheres.

Keywords: *Zirconia-silica composite, Nano particle, Corrosion-resistant coating, Mild steel, Composite, Fumed silica, SEM, XRD.*

1. INTRODUCTION

The upsetting things of corrosion on materials and configuration dictate the progress of corrosion-resistant materials. Corrosion not only exhibits significant safety concerns but also has a extensive economic influence, with calculated annual costs in the trillions. The results of corrosion can be far-reaching, out of the breakdown of vital configuration to the malfunctioning of devices and machineries. Hence, it is required to produce materials that can resist the corrosive influence of several ambiences.

Zirconia-silica composite materials propose a capable explanation, mixing the advantages of zirconia and silica to produce a strong and long-lasting material. On getting benefits out of these characteristics, zirconia-silica composites can support augmented corrosion opposition value, enhance mechanical strength, and upgrade longevity, establishing a lucrative provision for several industrial usages like aerospace, automotive, and construction, where corrosion resistance is pivotal.

Corrosion Management
ISSN: 1355-5243
(https://corrosion-management.com/)
Volume 35, Issue 02 – 2025
SCOPUS

Corresponding-author-email:
rupps28@gmail.com

Zirconia-silica composites are some kind of superior matters that unite the benefits of zirconia and silica, providing elevated magnitudes of corrosion resistance, mechanical attributes, along with thermal stability. These composites are tuned towards use in harsh ambient, like chemical processing, marine applications, on behalf of their corrosion-resistant attributes. In addition to it, their excellent mechanical features, like toughness, strength, etc. make them appropriate toward greater-functioning in industries like aerospace and automotive.

Zirconia-silica composites also promote upgraded thermal attributes, comprising greater thermal steadiness and opposition to thermal shock, making them desirable toward high-temperature usages namely heat exchangers, furnace components, and thermal barrier coatings. The goal of it is to produce a corrosion-resistant guard around mild steel through artificially producing zirconia-silica (ZrO2-SiO2) composite, setting as a usual layer on the steel outer part, and designating its microstructural and phase attributes via Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) choices.

2. LITERATURE SURVEY

The development of Zr-O-Si bonds upon the ceramic outer surface via tribochemical execution restricts deep migration of surface hydroxyl group, consequently upgrading corrosion opposition. Moreover, the settling of the tetragonal phase in ZrO_2-SiO_2 composite due to kinetic aspects also contributes to its enhanced corrosion resistance Dai, et al. (2021).

The production of epoxy coatings adds a hybrid mixing of SiO_2 and ZrO_2 nanoparticles, show upgraded mechanical and anti-corrosion characteristics, Samad, et al. (2023). The protective properties of organically modified silica (ORMOSIL)-zirconia coatings, specifically their corrosion and scratch resistance. The SiO_2/GPTMS/ZrO_2 coating significantly enhances corrosion resistance, with a polarization resistance 84 times higher than uncoated 316L steel, Gąsiorek, et al. (2021).

The use of sol-gel post-treatment methods to refine the porosity network of ZrO_2 coatings on 316L substrates, enhancing their corrosion resistance. The alkaline-catalysed TEOS solutions produce a dense, continuous SiO_2 interlayer, providing superior barrier performance compared to acidic-catalysed solutions, Khalesi, et al. (2021). Zirconium-based refractories are crucial in the glass industry due to their high refractoriness, thermal shock resistance, and corrosion resistance, but they still require periodic replacement due to wear and corrosion. chang, et, al (2024). The corrosion process of zirconium-based refractories in glass-contact areas, identifying areas for innovation and improvement, Perez Velasquez, et al. (2025). The use of SiO_2, ZrO_2, and SiO_2-ZrO_2 blend coatings on polycrystalline silicon solar cells, finding that the SiO_2-ZrO_2 blend coating achieved the peak efficiency of 17.6%. The blend coating demonstrated superior anti-reflective properties, with a low light reflectance of 6%, leading to enhanced photon transmittance and improved solar cell performance, Trabelsi, et al. (2024).

The composition and corrosion obstruction of SiO_2-TiO_2-ZrO_2-Bi_2O_3 coatings deposited on Ti6Al4V alloy via spin-coating. The coatings exhibited good corrosion resistance, reducing current densities by single unit, and demonstrated promising potential for protecting metal substrates from corrosion, Vega, et al. (2018). A superhydrophobic coating was developed using a spraying technique, combining γ-Methacryloyloxy-

Corrosion Management ISSN: 1355-5243
(https://corrosion-management.com/)
Volume 35, Issue 02 – 2025
SCOPUS

propyl-tri-methoxy silane (KH570)-modified ZrO_2/SiO_2/silicone-modified acrylic emulsion, Ben, et al. (2023).

The addition of amorphous SiO_2 to ZrO_2-SiO_2 composite coatings enhanced their properties by reducing porosity, increasing interlayer thickness, and improving corrosion resistance. The optimized coating composition exhibited a higher barrier effect and lower permeability, making it suitable for protective applications, Farhadian, et al. (2020).

3. MATERIALS AND METHODS

3.1 Preparation of Composite material from Zirconia and fumed silica:

1. Preparation of Nano Zirconia powder from Zircon concentrate:

Beach sand samples from India's eastern coast were processed using various separation techniques to recover zircon concentrate.Sunita.et.al. (2011)

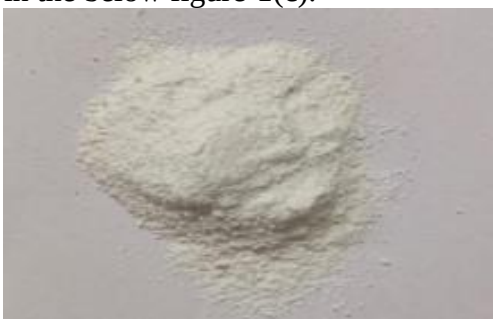
Zircon concentrate and sodium hydroxide flakes were heated at 650℃ in a muffle furnace. The cooled solid was treated with water and dilute HCl, yielding a clear solution. Precipitation with sulfuric acid produced a super white product, which was washed to remove sulphates. Finally, calcination generated ZrO_2 nanoparticles. The calcined nano ZrO_2 powder shown in the underneath figure-1(a). Sunita.et.al. (2021)

2. Synthesis of Zirconia-Silica Composite Materials:

The reaction is believed to occur through the following mechanism:

$$ZrO_2 + SiO_2 \rightarrow ZrSiO_4$$

The commercial fumed silica used for preparation is as shown in figure-1(b). The purified nano-zirconia powder was mixed with fumed silica in a 1:1 mol ratio. The mixture was ground and mixed thoroughly in a mortar. The zirconia-silica mixture was then calcined at different temperatures (1000°C, 1100°C, 1200°C, 1300°C, and 1400°C) in an alumina crucible with a lid. The calcination time was varied with different temperatures. The composite powder formed at 1400°C as shown in the below figure-1(c).



a) Nano ZrO2

b) Fuming SiO_2

c) ZrO_2-SiO_2 Composite at 1400°C

Fig. 1: ZrO_2, SiO_2 and its composite

Corrosion Management ISSN: 1355-5243
(https://corrosion-management.com/)
Volume 35, Issue 02 – 2025
SCOPUS

3.2. Application of the ZrO_2-SiO_2 composite powder for test corrosion resistance on the metal surface

The ZrO_2-SiO_2 composite material, synthesized at 1400°C, was mixed with a binder to enhance adhesion properties and form a uniform paste. The layered mild steel sample has demonstrated in the underneath figure 2.

Fig.2: ZrO_2 + SiO_2 Composite powder coated on Mild Steel surface

This paste was applied onto the surface of mild steel through multiple coating to achieve the desired thickness and uniformity. Following the coating process, the specimen underwent natural curing for 24 hours to facilitate proper binder setting and adhesion to the substrate. Subsequently, the coated specimen was subjected to heat treatment at 300°C in a furnace for 5hours. This thermal treatment was conducted to:

a. Improve adhesion between the coating and the metal substrate.

b. Enhance the mechanical properties of the coating.

c. Subtract volatile organic compounds (VOCs) exist in the binder.

3.3.Immersion Corrosion Testing of Coated sample :

Two mild steel specimens were surface-coated with a ZrO_2 + SiO_2 composite powder, and two uncoated mild steel specimens of identical dimensions (length: 4.0 cm, width: 1.5 cm, and thickness: 1.0 cm) were used as reference samples. The coated and uncoated specimens were separately immersed in seawater and 0.1 M sulfuric acid (H_2SO_4) solutions. After an exposure period of 168 hours, the samples were removed from the solutions and weight loss was analyzed.

4. RESULTS AND DISCUSSIONS

4.1.XRD Patterns of ZrO_2-SiO_2 Composite Calcined at Different Temperatures Calcined at 1100°C :

The consequence outcome of ZrO_2-SiO_2 composite was then figured using X-Ray Diffraction (XRD) study.

The XRD sample of the last produce has presented in the underneath picture. The outcomes expressed that only 5.6% of the last object was zircon, while the rest 94.4% being monoclinic zirconia.

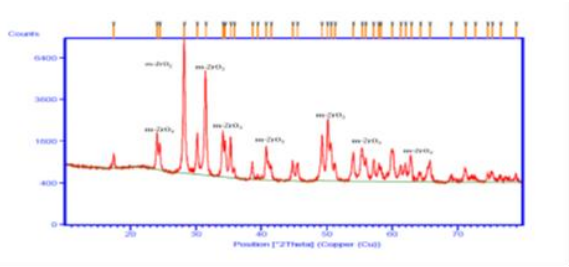


Fig. 3: XRD result at 1100°C

The sample exhibits certain peaks equivalent to the monoclinic segment of zirconia (ZrO_2). The peaks are grouped to the monoclinic zirconia stage, assuring the involvement of this state in the last produce. As a matter of fact, no peaks consequent to zircon ($ZrSiO_4$) were monitored in the XRD sample. This assures that the reaction between ZrO_2 and SiO_2 did not outcome in the settling of zircon, but rather led to the establishment of monoclinic zirconia segment.

Corrosion Management ISSN: 1355-5243
(https://corrosion-management.com/)
Volume 35, Issue 02 – 2025
SCOPUS

Table 1: XRD peak positions and orresponding phases

2θ (°)	d-spacing (Å)	Phase
24.2	3.67	Monoclinic ZrO_2
28.2	3.15	Monoclinic ZrO_2
31.5	2.83	Monoclinic ZrO_2

Calcined at 1200°C:

The outcome produces of ZrO_2-$SiO_2$was then designated implementing X-Ray Diffraction (XRD) study. The XRD sample of the last produce is exhibited in picture 4. The sample expresses peaks related to both tetragonal zircon ($ZrSiO_4$) and monoclinic zirconia (ZrO_2) states. The peaks are sorted to the corresponding phases, setting the existence of both phases in the last object. The comparative magnitudes of zircon and zirconia phases in the last object were accounted considering the XRD peak intensities.

Table 2: XRD peak positions and corresponding phases.

2θ (°)	d-spacing (Å)	Phase
20.2	4.39	Tetragonal $ZrSiO_4$
24.2	3.67	Monoclinic ZrO_2
28.2	3.15	Monoclinic ZrO_2
31.5	2.83	Monoclinic ZrO_2

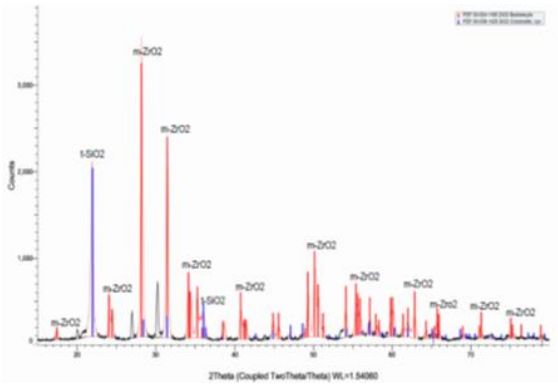


Fig: 4: XRD result at 1200°C

The XRD outcomes pointed out that the interaction between ZrO2 and SiO2 at 1200°C consequent in the development of both tetragonal zircon and monoclinic zirconia phases. The reduce percentage of zircon production recommends that the reaction environment may not have been fine tuned for highest zircon generation.

Calcined at 1400°C:

The composite of ZrO_2-SiO_2 arranged at 1400°C comprising 66.2% ZrO2 and 28.76% SiO2.The XRD sample exhibited sharp peaks, with the highest intensity consequent to the tetragonal zircon phase. The control of tetragonal zircon peaks in the XRD sample recommends that the interaction preferred the creation of this phase. The augmented interaction time and temperature may have contributed to the risen preparation of the tetragonal zircon phase.

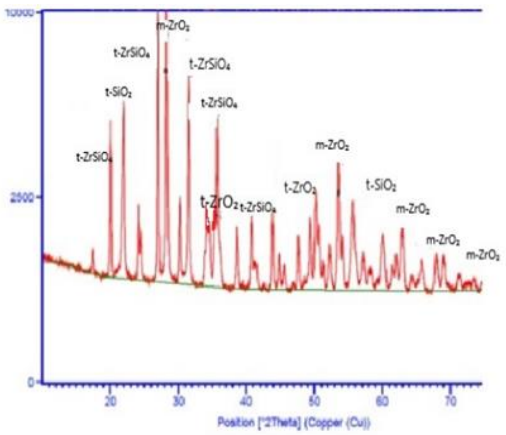


Fig: 5: XRD result at 1400°C

Table3: XRD peak positions and corresponding phases

2θ (°)	d-spacing (Å)	Phase
20.2	4.39	Tetragonal $ZrSiO_4$
22.5	3.94	Tetragonal $ZrSiO_4$
24.2	3.67	Monoclinic ZrO_2
28.2	3.15	Monoclinic ZrO_2

Corrosion Management ISSN: 1355-5243
(https://corrosion-management.com/)
Volume 35, Issue 02 – 2025
SCOPUS

4.2.TEM study of the composite 1400℃ :

The elemental magnitude of the composite ZrO_2-SiO_2 tested in Transmission electron microscope (TEM).

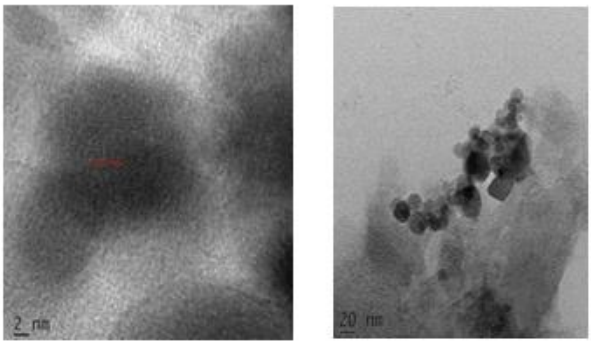


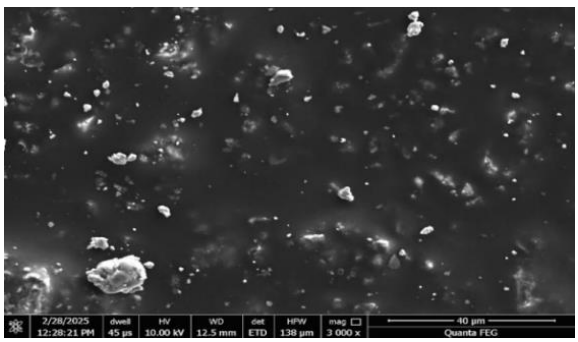
Fig: 6: TEM analysis of Composite ZrO_2-SiO_2 at 1400℃

The XRD and TEM analysis confirmed the production of nano-particle size zirconia from beach sand. The XRD, SEM and TEM analysis of the composite materials revealed the formation of a zirconia-silica composite phase.

4.3 Characterization of Coated Composite Materials:

The produced composite materials coated on metal surface were characterized using SEM analysis to determine their phase composition and crystallinity.

SEM Observations:



(a)

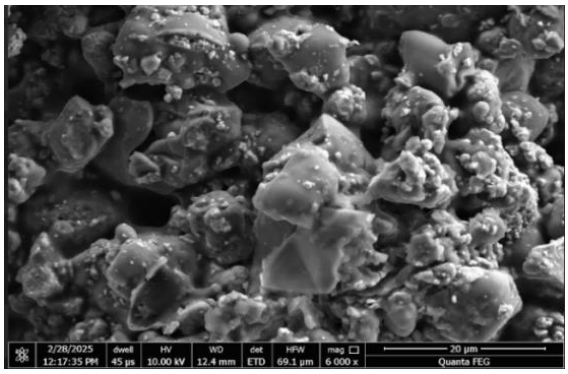


Fig. 7 (a) & (b SEM of coated ZrO_2+SiO_2

(a) The packed and crack-free layering can diminish the corrosion rate by reducing the revelation of the substrate to corrosive samples.

(b) In addition to this the existence of ZrO_2 and SiO_2 particles can enhance the coating's obstruction attributes, diminishing the dispersion of corrosive species and ions.

(c) The regular layering thickness and sound adhesion can also enhance the coating's reliability, diminishing the threat of delamination along with corrosion.

(d) In addition, the uniform dispersion of ZrO_2 and SiO_2 elements can diminish the threat of pitting corrosion by reducing the development of localized corrosion cells.

In a nutshell, the layer's composition and microstructure can raise passivation, dropping the threat of corrosion start and propagation, and consequently leading to modified corrosion resistance.

4.4.Weight loss in Immersion test of Mild steel with and without coating of Composite ZrO_2-SiO_2

Table4: Corrosion rate of Mild steel with & without coating in **S**ea water (3.5%NaCl solution)

Sea Water Immersion Test	Mild Steel without coating	Mild Steel Coated with composite ZrO_2&SiO_2
Time(hr)	168	168
Loss In Weight of Sample (mg/cm^2)	2.23	0.0005
Corrosion rate mm/year	0.14	0.004

Table4 and Table-5 the weight loss calculated from the initial and final weight of the sample before and after treatment for 168hrs.Corrosion rate was calculated using the below formula
Corrosion Rate (mm/yr) =

$$\frac{87.6 \text{ X Weight loss of Sample}}{\text{Density of Mild steel X Area X time}}$$

Table5: Corrosion rate of Mild steel with & without coating in 0.1M H_2SO_4 acid Solution

0.1M H_2SO_4 acid Solution Immersion test	Mild Steel without coating	Mild Steel Coated with composite ZrO_2&SiO_2
Time(hr)	168	168
Loss In Weight(mg/cm2)	5.17	0.006
Corrosion rate (mm/year)	6.68	0.001

From the results presented in Tables 4 and 5, the corrosion rate of the bare mild steel specimen is 0.14 mm/year in seawater, whereas the coated sample exhibits a significantly lower corrosion rate of 0.004 mm/year. In 0.1 M H_2SO_4 solution, the corrosion rate of mild steel increases to 6.68 mm/year, while the coated specimen shows a markedly reduced corrosion rate of only 0.001 mm/year.

5. CONCLUSION

This work exhibits the soundness of zirconia-silica (ZrO_2-SiO_2) composite coatings in rising the corrosion resistance of mild steel. The artificially prepared composite, developed via mixing nano ZrO_2 and fumed SiO_2 in a 1:1 molar ratio and calcined at temperatures up to 1400°C, demonstrated a secure crystalline configuration with monoclinic ZrO_2 and tetragonal $ZrSiO_4$ states. X-ray diffraction (XRD) established finest phase development, while scanning electron microscopy (SEM) showed a steady, closely packed, and crack-free layering with tough adhesion to the metal substrate.The corrosion rate with coating of composite ZrO_2-SiO_2 in sea water 0.001mm/yr and in 0,1M solution 0.004mm/year. The composite layering considerably enhanced resistance to corrosion in harsh ambience, diminishing the influence of acids, salts, and moisture. These outcomes underscore the potential of ZrO_2-SiO_2 composite layering's for industrial usages, specifically in aerospace, automotive, and marine sectors, where reliability and corrosion resistance are pivotal. Further tuning of coating attributes and reliability examining can raise its functioning, setting it a possible safe-guard solution against distinct engineering usages.

Future works can concentrate on tuning the layering practice, assessing the long-term corrosion resistance of the layered steel, and showcasing the possible of this coating for other substrate objects. Additionally, the mechanical characteristics of the layering, like adhesion soundness and scratch resistance, can be tested to further realize its function and reliability aspects.

Acknowledgement: The authors acknowledge 'National Seminar on Corrosion and its Prevention- Oil & Gas Industry' CPOG-2025, C.V. Raman Global University in collaboration with AMPP India Chapter.

6. REFERENCES

[1] Dai, S., Fu, J., Lei, H., & Chen, Y. (2021). Study on the interaction between SiO2 and ZrO2 in the chemical mechanical polishing of zirconia ceramic with colloidal silica. Ceramics International, 47(15), 21642-21649.

[2] Samad, U. A., Alam, M. A., Abdo, H. S., Anis, A., & Al-Zahrani, S. M. (2023). Synergistic effect of nanoparticles: enhanced mechanical and corrosion protection properties of epoxy coatings incorporated with SiO2 and ZrO2. Polymers, 15(14), 3100.

[3] Gąsiorek, J., Mazur-Nowacka, A., Szczurek, A., Babiarczuk, B., Tic, W. J., Guziałowska-Tic, J., & Krzak, J. (2021). Influence of zirconia and organic additives on mechanical and electrochemical properties of silica sol-gel coatings. Materials, 14(9), 2389.

[4] Khalesi, F., Farhadian, M., &Raeissi, K. (2021). Porosity tailoring of electrophoretically derived zirconia coatings using acidic and alkaline-based sol-gel post-treatment to enhance anti-corrosion performance. Surface and Coatings Technology, 425, 127692.

[5] Perez Velasquez, C., Montazerian, M., & Mauro, J. C. (2025). Corrosion of zirconium‐based refractories in glass‐contact areas: Mechanisms and challenges. International Journal of Applied Ceramic Technology, e15064.

[6] Trabelsi, A. B. G., Kaliyannan, G. V., Gunasekaran, R., Rathanasamy, R., Palaniappan, S. K., Alkallas, F. H., ... & Mostafa, A. M. (2024). Surface engineering of Sio2-Zro2 films for augmenting power conversion efficiency performance of silicon solar cells. Journal of Materials Research and Technology, 28, 1475-1482.

[7] Vega, F. L. A., Olaya, J. J., & Ruiz, J. B. (2018). Synthesis and corrosion resistance of SiO2-TiO2-ZrO2-Bi2O3 coatings spin-coated on Ti6Al4V alloy. Ceramics International, 44(2), 2123-2131.

[8] Ben, J., Wu, P., Wang, Y., Liu, J., & Luo, Y. (2023). Preparation and Characterization of Modified ZrO2/SiO2/Silicone-Modified Acrylic Emulsion Superhydrophobic Coating. Materials, 16(24), 7621.

[9] Farhadian, M., Raeissi, K., Golozar, M. A., Labbaf, S., Hajilou, T., &Barnoush, A. (2020). 3D-Focused ion beam tomography and quantitative porosity evaluation of ZrO2-SiO2 composite coating; amorphous SiO2 as a porosity tailoring agent. Applied Surface Science, 511, 145567.

[10] Patent CN102224106A Fillers and composite materials with zirconia and silica.

[11] Sunita R and R. Bhima R (2011) Beneficiation and Characterization of Detrital Zircons from Beach Sand and Red Sediments in India, Journal of Minerals & Materials Characterization & Engineering, Vol. 10, No.15, pp.1409-1428.

[12] Sunita Routray, Rupambika Mohanty, Ranjita Swain, Silani Sahu & B. R. Mishra, “Preparation and Characterisation of Zirconia Nano-materials Prepared From Zircon Minerals of Brahmagiri Coast”,J.Inst. Eng. India Ser. E (June 2021) 102(1):87–95, https://doi.org/10.1007/s40034-020-00201-1.

[13] Chang, CH., Lin, CY., Chang, CH. et al. Enhanced biomedical applicability of ZrO2–SiO2 ceramic composites in 3D printed bone scaffolds. Sci Rep 12, 6845 (2022). https://doi.org/10.1038/s41598-022-10731-w.

[14] Kesmez O, ¨ Akarsu E, Çamurlu HE, Yavuz E, Akarsu M, Arpaç E. Preparation and characterization of multilayer anti-reflective coatings via sol-gel process. Ceram Int 2018;44:3183–8