Journal of Ceramic Processing Research. Vol. 25, No. 6, pp. 931~936 (2024)
(Received 28 March 2024, Received in revised form 16 July 2024, Accepted 13 August 2024)
https://doi.org/10.36410/jcpr.2024.25.6.931

JOURNAL OF
Ceramic
Processing Research

Influence of graphene reinforced inside yttria stabilized zirconia in terms of functional & mechanical properties

P. Ganeshan[a,*], **T. Rajesh**[b], **Bipin Kumar Singh**[a] **and K. Raja**[c]
[a]*Centre for Augmented Intelligence and Design, Department of Mechanical Engineering, Sri Eshwar College of Engineering, Coimbatore-641202, Tamil Nadu, India*
[b]*Department of Mechanical Engineering, Mangayarkarasi College of Engineering Paravai, Madurai-625402, Tamil Nadu, India*
[c]*Department of Mechanical Engineering, Anna University Regional Campus Coimbatore, Coimbatore-641046, Tamil Nadu, India*

The study focused to explore the effect of graphene (rGO) (0.3 wt.%) inside the yttria-stabilised zirconia (YSZ) matrix in terms of mechanical and functional properties. The samples were developed through the powder metallurgy route. The requisite amounts of powders were uniaxially pressed in disc shapes having 20 mm diameter and sintered at 1350 °C for half an hour in HT furnace. The sintered samples were thoroughly polished till the average surface roughness reached to 0.5 micron. The microstructure analysis revealed that the presence of graphene acts as a grain refiner result in homogeneous structure of grain morphology throughout the structure. Additionally, the presence of graphene significantly improved fracture toughness by 21% without compromise in hardness. The improvement was attributed to the refinement in gain morphology accompanied by crack bridging or deflection. The functional analysis revealed that the co-efficient of friction for 0.3 wt.% rGO inside YSZ improved by 20% compared to simple YSZ. A thin film formation (transfer film) developed between the interacting materials is responsible for the improvement in the co-efficient of friction. Hence, the developed ceramics that have excellent fracture toughness and tribological properties may suitably applied for production of ceramic seals.

Keywords: Graphene (rGO), Yttria Stabilized Zirconia (YSZ), Hardness, Fracture toughness, Coefficient of friction.

Introduction

Superior mechanical properties with low functional properties are highly acknowledged by industries due to possession of prolongs life and efficient performance of the component. In this advent researchers found that ceramics composites showed huge potential to meet the expectation. However, the brittleness of ceramics that restricts its application is major challenge for the scientific community. Later, the research on zirconia ceramics, doped with yttria showed huge improvement in fracture toughness as well as mechanical properties due to phase transformation [1, 2] aligned with transformation toughness mechanism [3]. The mechanism leads to relive stresses at different temperature that provide better behaviour of ceramic composites. Further restriction of zirconia ceramics comes from its poor functional properties i.e. high co-efficient of friction (COF) that limit the life of component as well as efficiency. Therefore, to enhance the functional properties researchers developed a new class of ceramics i.e. doping yttria stabilised zirconia (YSZ) with various additives such as graphene [4], CaF_2 [5] and CuO [6, 7] called as self lubricating ceramics [8]. Among the various additives due to outstanding mechanical properties, large specific surface area, excellent chemical stability and high aspect ratio of graphene [9] attracts the researchers to study its application in ceramic matrix.

Study carried by Liu et al. [10] explained the enhancement in toughness due to addition of graphene in zirconia/alumina composites. The research also revealed that with 0.81 vol% GPLs into ZTA composites, the fracture toughness was improved by 40%. The mechanism suggested that the pull-out of GPLs lead to crack bridging and crack deflection phenomenons responsible for improvement in mechanical properties. Later, Shin et al. [11] investigated thorough investigation on the beneficial effect of graphene oxide inside yttria-stabilized zirconia composite. The results showed significant improvement of the mechanical as well as electrical properties. The RGO had low shear resistance properties easily pull-out from matrix, lead to enhancement in crack bridging mechanism that contributed towards improvement in fracture toughness. Su et al. [12] reinforced graphene nanosheet inside yttria-stabilized zirconia to investigate scratch test and mechanical properties. The result showed that with addition of graphene the elastic property hardness and toughness were improved by 18%, 13% and 36% respectively. The phenomenons that were responsible for the improvement in toughness are GNS pullout, GNS bridging, crack deflection, and

---

*Corresponding author:
E-mail: ganeshram84@gmail.com

crack branching. The investigations also concluded that a tougher TZP composite induced by the added GNSs protects it from severe scratch by brittle micro-fracture to improve the frictional coefficient. Feng et al. [13] developed graphene nanosheets/Al_2O_3+13 wt%TiO_2 for coating on 304 stainless steel through plasma spraying. Researchers observed an improvement of ~13% and ~19% in COF (Coefficient of friction) and wear rate respectively. The analysis carried out through energy dispersive spectrometer (EDS) and Raman spectroscopy strongly confirm the transfer layer mechanism i.e. graphene layer formed on the wear scar surface act as protective and lubricating layer; result in improvement of functional properties. Ramesh et al. [14] investigated the mechanical properties of graphene oxide-doped Y-TZP ceramics through pressure less sintering at different temperature (1200 °C to 1500 °C). Researchers observed that the maximum hardness i.e. 14.3 GPa was achieved at a temperature of 1300 °C whereas, the maximum fracture toughness i.e. 5.6 MPa·$m^{1/2}$ was observed at 1400 °C. Finally researchers concluded that the beneficial effect of rGO was observed for lower sintering temperature. Wu et al. [15] demonstrated the surface state of graphene film during evaluation of COF. Researchers demonstrate that the presence of graphene generated a more pronounced luminescence response during frictional test responsible for the improvement in functional properties. Zhang et al. [16] demonstrated a remarkable improvement of 200% and 41% in bending strength and fracture toughness respectively, by doping 3Y-ZrO_2 with 0.15 wt% GO. Again the researchers demonstrated that the Crack deflection, crack bridging, and GO pull-out were predominant mechanism that responsible for improvement in mechanical properties.

Furthermore the recent application of rGO doped ceramics towards improvement of functional properties was shown by numerous of researchers [17, 18] but still the physics behind the improvement is inconclusive and needed through study. Hence in this work an htrough attempt to demonstrate the behavior of graphene (rGO) as an additive is thoroughly studied and compared with reference 3Y-ZrO_2 matrix. The comparative study is carried out in terms of mechanical as well as functional properties to provide better understanding on application of rGO as an additive in commercial application.

Procedures Followed to Carry Out Experiments

Preparation of composites

In this investigation, yttria stabilized zirconia (YSZ) powders (average particle size: 90 μm, supplier Artha), was selected as reference composite, reinforced with reduced 0.3 wt.% graphene oxide (rGO). At first, the requisite amount of rGO was kept in a beaker and thoroughly dispersed using probe-sonicator in a wet medium to mitigate the agglomeration inside the structure. The well dispersed rGO and YSZ powders were placed in a planetary ball-mill having zirconia jar with 0.8% polyethylene glycol (as a Plasticizer). The wet milling of the respective elements were carried out using high purity zirconia balls of varying diameters (8-10 mm) 24 hr to get a homogeneous mixed composite. Ball milling applied repeated collision of grinding media (balls) within a milling chamber to achieve a fine particle size and mix materials a widely used technique in materials science and engineering for the preparation of composite materials. This process entirely useful for the particle size reduction and distribution of grains inside the cluster of matrices. In earlier work of authors group [19] the milling process was optimized through selecting several milling speed and analyses its effect on the mechanical properties of ZTA composites. The milled composites were kept at high temperature atmosphere (120 °C) using clean oven for 24 hr. After complete drying the lumped were gently crushed in a mortar pestle to get a fine powder. The fined mixed powders were further treated at high temperature 800 °C for soaking time 2 hr in order to remove all organic items. The calcined powders were used for sample preparation and grain size evaluation.

Sample Preparation

The preparation of samples plays vital role on the end properties, so all standards as per ASTM were maintained during fabrication of samples. The fabrication of samples starts with requisite amount of 0.3 wt.% rGO/YSZ calcined powders, mixed with 5 wt.% PVA (polyvinyl alcohol) (act as binder) solution in automatic stirrer for 60 min. The mixed wet powders were placed at 100 °C in an oven for 6 hr to eliminate the water content of the binder solution. Green compaction of dried powder was done in a hydraulic press with a die-punch arrangement. The discs type samples having diameter of 20 mm, each weighing 14 g were prepared by pressing at a pressure of 5 ton cm^{-2}. After pressuring the green samples were gently push out from the die and kept in a ceramic crucible. After placing the samples the crucible was full with alumina power to get better densification. The covered crucible was then decomposed to high temperature i.e. 1350 °C for half an hour in HT furnace. Sintering is a crucial stage in the processing of ceramic materials where powders are heated to form a solid, dense structure. Hence, temperature plays a significant role in the sintering process, affecting various properties and outcomes of the final ceramic products. If the material is not fully sintered it mechanical properties are degraded to larger extent, so, it is important to select right temperature [20]. The heating rate was maintained as 10 °C/min up to 600 °C; 8 °C/min up to 1000 °C; 4 °C/min up to 1200 °C; 3 °C/min up to 1350 °C. The cooling rate was 10 °C/min until the inertia of the furnace prevailed. After cooling the samples were removed from crucible and went under finishing processes. The finishing processes start with lapping process with three different mesh sizes of silicon carbide (400, 600 and 800) powders on a glass plate. The semi finish samples were thoroughly washed and sonicated to remove the impurities present or adhere on the surface. After thorough cleaning the samples were placed on Bain polisher to polish with diamond paste under kerosene as wet media. The polishing operation carried out till the surface roughness not come under 0.5 micron. Again the polished samples were properly washed and sonicated to remove the foreign elements from the surface. After policing the samples were decomposed at 800 °C to relive inbuilt stresses. The heated samples after cooling were used to investigate the mechanical and functional properties.

Evaluation of mechanical and functional properties

The characterization of samples starts with the evaluation of microstructure of sintered samples. After sintering the samples were used to evaluate the FESEM images (CARL-ZEISS-SMT-LTD, Germany, Model: SUPRA 40) to know the grain morphology. After evaluation of FESEM images the crystalline phases were studied by XRD- PW1710 with Cu-Kα radiation (λ= 0.15406 nm). The range of 2θ was maintained between 20-70° at an angular step of 0.02°. The crystalline phases of zirconia were studied with special attention as the phases have significant contribution on transformation toughening mechanism. After morphological studies Vickers hardness testing machine was used to evaluate the hardness and indentation fracture toughness of polished samples. The properties were evaluated using Eq. (1) & (2) [19].

$$HV=1.854(F/D^2) \tag{1}$$

$$K_{IC}=0.16(c/a)^{-1.5}\ (Ha^{0.5}) \tag{2}$$

Where, HV=Vickers hardness (MPa), K_{IC}=Fracture toughness (MPa·$m^{1/2}$), F=applied load (Kgf), D^2=area of the indentation (mm^2), H=Test load (Newton), c= Average length of the cracks obtained at the tips of the Vickers marks (microns), a=Half average length of the diagonal (microns).

The objective of this work is to demonstrate a clear comparative study between rGO/YSZ and YSZ in terms of functional properties to understand the physics behind behavioural changes. Therefore, the coefficients of friction (COF) for developed samples were carried out using ball on disc tribometer. A load of 20 N and sliding velocity of 4 mm/sec was maintained during the experiments. Zirconia balls having 8 mm sizes were used as counter surface for a run of 4000 sec. After testing the SEM images of wear track for both the samples were taken at same magnification to understand the phenomenons that affect the functional properties. A though investigation, correlated with earlier finding has been illustrated for better application of such composites. The scar diameter developed on the counter surface was used to evaluate the specific wear rate [21].

Result and Discussion

In ceramics grain morphology and densification have huge impact on the end properties and its behavioural changes at different parameters. So, the investigation starts with grain morphology evaluation using FESEM images. The sintered samples were directly used to capture FESEM images which are shown in Fig. 1(a) and (b). The magnification of capturing the images was kept constant for both composites i.e. YSZ and 0.3 wt.% rGO/YSZ in order to understand the effect of graphene. From FESEM images it is observed that the composites formed are homogeneous and highly dense. The analysis on grain morphology illustrate that the average grains sizes are refined and decreased with incorporation of graphene particle. The study carried out by Liu et al. [22] showed that the formation of grains align with the pore mobility rate during densification process. Researchers demonstrated that the mobility of pores being dragged were entirely dependent on the amount of porosity and the driving pressure. The properties of particles that restrict the pore surface diffusion as well as controlled the motion result in uniform formation of grain inside

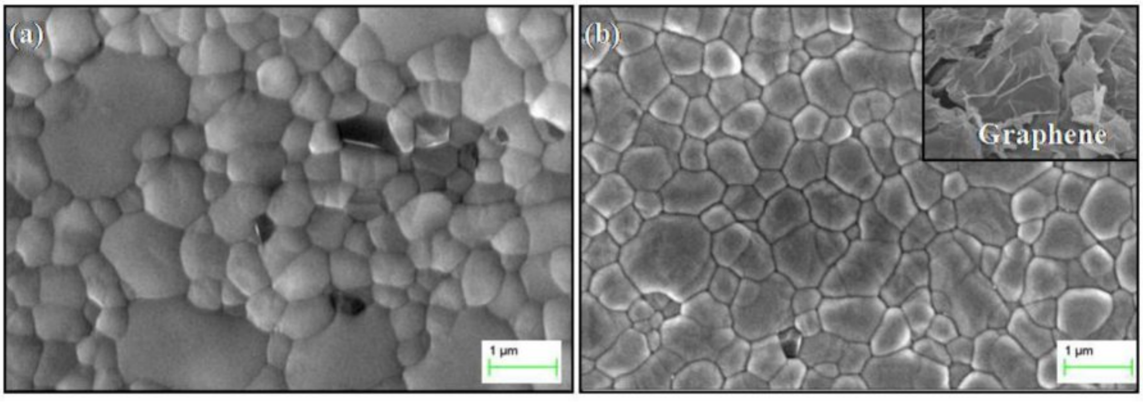

Fig. 1. (a) FESEM image of YSZ (b) FESEM image of 0.3 wt.% rGO/YSZ.

the cluster. So, it was observed that the presence of graphene exaggerated the diffusion-controlled motion at the time of sintering may result in uniform formation of grain throughout the structure. Furthermore, the refining of grain structure due presence of graphene inside the cluster was also cited by Liu et al. [23]. In the said experiments researchers break the bulk sintered samples to delve that the presence of graphene refines the grain morphology of zirconia cluster. Hence it can be concluded that the presence of graphene act as a grain refiner inside the cluster.

Mechanical Properties

The end properties of ceramic composites are entirely dependent on densification and grain morphology, developed inside the cluster. The stable graphene structure, inside the cluster generally showed high end properties [24]. The FESEM images of developed composites show homogeneous and densely packed structure. The analysis also observed that the average grain sizes of YSZ are greater than 0.3 wt.% rGO/YSZ. So, the reflection of grain morphology is observed on mechanical properties i.e. hardness almost same whereas, the fracture toughness is significantly improved by 21%. The evaluated values of hardness and fracture toughness are shown in Fig. 2(a) and (b). The small improvement in hardness is attributed to the grain refinement and formation uniform grain sizes inside the cluster due to presence of graphene particle.

The earlier research dedicated on toughening phenomenon illustrates [25] that crack-bridging, branching, deflection and transformation toughening, are the predominant mechanism that have potential to significantly augment the toughness of composite. Hence, the additives that have capability to improve the said phenomenon lead to high toughness materials. The researchers on graphene clearly demonstrate that it has high surface area, tough, flexible, high strength and ease to deform. The said properties make its competence for easy bonding between graphene and ceramic matrix. The bonding enhances the interfacial friction within the matrix result in consumption of higher stress lead to obstruction for propagation of crack [26]. The said phenomenon is known as crack bridging or deflection.

Furthermore, the direct correlation between fracture toughness and grain sizes was demonstrated by Yao et al. [27]. Researchers observed that when grain sizes increased beyond 0.5 μm it negatively impact the fracture toughness. So, YSZ had larger grain sizes reflect in minimum fracture toughness. So, weak bonding interfaces and uniform grain sizes created inside the matrix (due to presence of reinforcing phase graphene) result in high fracture toughness.

Functional Properties

The ceramics composites the properties that significantly contribute on frictional behaviors [28] are sliding velocity, surface condition, pressure, applied loads and temperature. Apart from the said properties researchers found that if the surface condition during interaction is improved the frictional factor also improved. So, the said behaviour can be improved by contamination or generation of any oxide layers between the interacting surfaces during sliding. The formation of oxide layers can be exaggerated by reinforcing the foreign materials that have low shear strength (easily deform) and high adhesiveness [29]. The said properties are governed by graphene which makes it compatible to use as solid lubricant. Hence, the intention of this researcher is to reinforced graphene as solid lubricant inside YSZ matrix, to improve the tribological properties. The tribological property in terms of coefficient of friction is shown in Fig. 3. From, Fig. 3 a clear improvement in COF by 20% due to presence of 0.3 wt.% rGO inside YSZ is observed. The findings are in aligning with the result

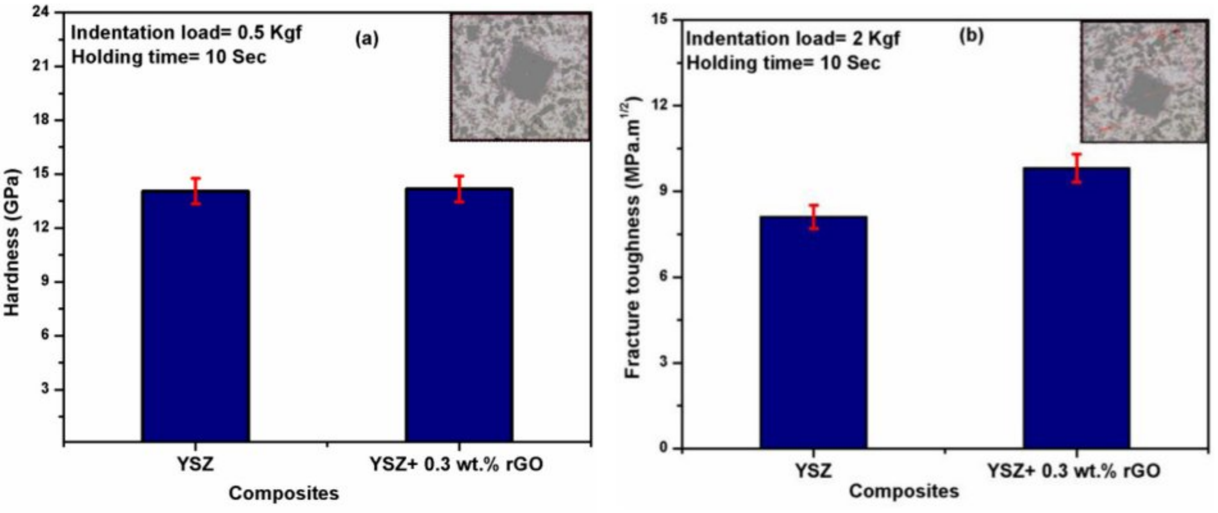

Fig. 2. (a) Evaluated values of Hardness, (b) Evaluated values of Fracture Toughness.

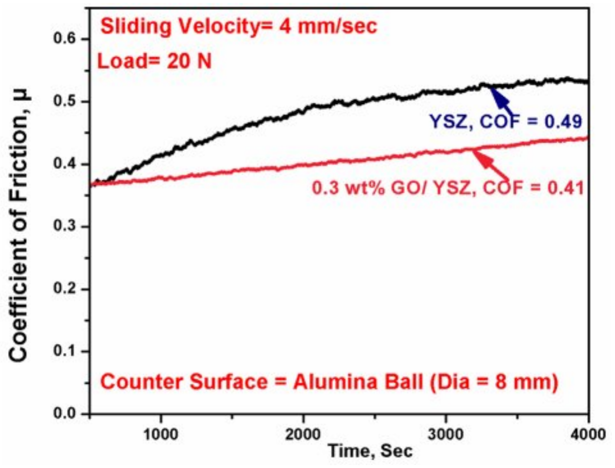

Fig. 3. Comparative study in terms of COF for 0.3 wt.% rGO/ YSZ and YSZ.

cited by Zang et al. [30]. Researchers demonstrate that the formation of transfer film at counter surface during interaction responsible for improvement in the frictional properties. Researchers demonstrate that the micro-ploughing and plastic deformation of particle lead to expose of graphene particles with counter surface. As, graphene have low shear strength and high surface area, tendency to adhere on the counter surface. The adhesion of graphene grains on counter surface develops a very thin film between the interacting surfaces responsible for the separation sliding surfaces. Hence, the said mechanism is known as transfer film phenomenon. Wang et al. [31] also illustrated similar mechanism for alumina doped graphene.

Conclusion

Homogeneous 0.3 wt.% rGO/YSZ composites were successfully prepared though powder metallurgy route. Beneficial effect of graphene, act as grain refiner was observed from the microstructure analysis. An improvement in fracture toughness by 21% without affecting the hardness was also observed. The refinements in gain morphology accompanied by crack bridging or deflection were responsible mechanism towards improvement in fracture toughness. Furthermore, the thin film formation (transfer film) due to presence of graphene particle results in improvement of COF by 20%.

Acknowledgement

The author thanks the Principal and Director of Sri Eshwar college of Engineering for their continual support to write this article.

Funding:

Fund received by DST-INDIA-FIST Program-2022 [TPN-83971] (SR/FST/College-/2022/1300).

Conflicts of interest/Competing interests

No conflict between the authors.

Availability of data and material

All data are presented in the manuscript.

References

1. K. Raja, P. Ganeshan, B.K. Singh, R.K. Upadhyay, P. Ramshankar, and V. Mohanavel, Sādhanā 48[2] (2023) 72.
2. K. Raja, M. Dhanabal, B.K. Singh, and P. Ganeshan, J. Ceram. Process. Res. 25[1] (2024) 79-84.
3. P. Ganeshan, Y. Sravani, K. Raja, and B.K. Singh, J. Ceram. Process. Res. 24[5] (2023) 781-787.
4. J. Su, Y. Chen, and Q. Huang, Appl. Phys. A 123[10] (2017).
5. G. Wu, C. Xu, G. Xiao, M. Yi, Z. Chen, and L. Xu, Int. J. Refract. Met. Hard Mater. 56 (2016) 51-58.
6. B.K. Singh, A.A. Yaduvanshi, and A.K. Mishra, In: Mukherjee, K., Layek, R.K., De, D. (eds) Tailored Functional Materials. Springer Proceedings in Materials, vol 15. (2022). Springer, https://doi.org/10.1007/978-981-19-2572-6_28
7. G. Gokilakrishnan, B.K. Singh, and M. Vigneshkumar, J. Ceram. Process. Res. 24[4] (2023) 655-661.
8. B.K. Singh, Trans. Indian Ceram. Soc. 82[1] (2023) 1-13.
9. M. Kukielski, A. Kasprzak, R. Zurowski, J. Tanska, P. Wiecinska, A. Wieclaw-Midor, J. Zygmuntowicz, M.A. Grigoroscuta, and P. Wiecinski, Powder Technol. 431 (2024) 119089.
10. J. Liu, H. Yan, M.J. Reece, and K. Jiang, J. Eur. Ceram. Soc. 32[16] (2012) 4185-4193.
11. J.H. Shin and S.H. Hong, J. Eur. Ceram. Soc. 34[5] (2014) 1297-1302.
12. J. Su, Y. Chen, and Q. Huang, Appl. Phys. A 123 (2017) 1-11.
13. Y. Feng, J. Fang, J. Wu, K. Gu, and P. Liu, Tribol. Int. 146 (2020) 106233.
14. S. Ramesh, M.M. Khan, H.A. Chee, Y.H. Wong, P. Ganesan, M.G. Kutty, U. Sutharsini, W.K. Chew, and A. Niakan, Ceram. Int. 42[15] (2016) 17620-17625.
15. H. Wu, K. Huang, J. Li, F. Jiang, X. Zhao, L. Wang, and S. Jiang, RSC Adv. 8[3] (2018) 1436-1442.
16. X. Zhang, C. Sun, H. Ji, M. Yang, H. Zhang, W. Tian, Y. Wu, O.V. Tolochko, and Y. Wang, JMST 167 (2023) 27-49.
17. W. Deng, X. Zhao, Y. An, J. Chen, and H. Zhou, Surf. Eng. 36[10] (2020) 1097-1106.
18. Y. Li, F. Chen, Q. Shen, and L. Zhang, Mater. Res. Express 6[9] (2019) 095080.
19. S.K. Gautam and B.K. Singh, Mater. Chem. Phys. 314 (2024) 128813.
20. B.K. Singh, A. Kumar, R. Cep, A. Kumar, A. Kumar, N. Dogra, and K. Logesh, AIP Adv. 14[8] (2024) 085207.
21. Y. Liu and B. R. Patterson, Metall. Mater. Trans. A 25 (1994) 81-87.
22. J. Liu, H. Guo, Y. Su, L. Wang, L. Wei, G. Yang, Y. Yang, and K. Jiang, Mater. Sci. Eng. A 688 (2017) 70-75.
23. Y.H. Huang, D.L. Jiang, X.F. Zhang, L. Zhenkui, and H. Zhengren, J. Eur. Ceram. Soc. 38 (2018) 4329-4337.
24. D.K. Shum and J.W. Hutchinson, Mech. Mater. 9[2]

(1990) 83-91.
25. M. Kostecki, M. Grybczuk, P. Klimczyk, T. Cygan, J. Woźniak, T. Wejrzanowski, L. Jaworska, J. Morgiel, and A. Olszyna, J. Eur. Ceram. Soc. 36 (2016) 4171-4179.
26. A.K. Srivastava, B.K. Singh, and S. Gupta, Evergreen 10[03] (2023) 1357-1365.
27. W. Yao, J. Liu, T.B. Holland, L. Huang, Y. Xiong, J.M. Schoenung, and A.K. Mukherjee, Scr. Mater. 65 (2011) 143-146.
28. S. Ganeshkumar, B.K. Singh, S.D. Kumar, S. Gokulkumar, S. Sharma, K. Mausam, C. Li, Y. Zhang, and E.M. Tag Eldin, Materials 15[22] (2022) 7994.
29. B. Vinith, S.D. Dharshan, S. Aravind, and B.K. Singh, IJIDeM 17[4] 2023 1443-1458.
30. C. Zhang, Z. Jiang, and L. Zhao, Surf. Topogr.: Metrol. Prop. 8[3] (2020) 035010.
31. X. Wang, J. Zhao, E. Cui, H. Liu, Y. Dong, and Z. Sun, Ceram. Int. 45[17] (2019) 23384-23392.