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Microstructural Characteristics of CuO Nanoparticles Incorporated Ceria-Yttria Stabilized Zirconia in Thermal Barrier Coating

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A B S T R A C T

Thermal barrier coatings are of great importance in the automobile industry for enhancing the performance of internal combustion engines. These coatings contribute significantly to such improvements without interfering with the design aspects of internal combustion engines. In this manuscript, an attempt has been made to study the characteristics of ceria-yttria stabilized zirconia incorporated with CuO nanoparticles, which are intended for use as thermal barrier coatings. Structural modifications and changes in grain patterns were identified using Scanning Electron Microscopy. The variations in the microstructural characteristics of the thermal barrier coatings were observed by varying the substitution percentage of CuO nanoparticles from 0.25% by weight to 1% by weight. The improvement in heat resistance capability upon incorporating CuO nanoparticles was investigated.

Keywords: thermal barrier coatings, CuO nanoparticles, microstructural investigation, Scanning Electron Microscopy.

1. Introduction

In recent times, significant developments have occurred in the field of automobile engineering. Numerous design changes and structural modifications have been implemented to enhance the performance of internal combustion engines. The process of making design modifications is highly complex and costly, involving a substantial amount of trial and error with precision. This is where thermal barrier coatings come into play, effectively improving the overall performance of internal combustion engines by retaining the thermal energy generated by the engine for an extended period. The internal surfaces of engine valves, cylinders, and piston walls can easily be coated with ceramic-based thermal barrier coatings to enhance engine performance. Recently, extensive research has been conducted to improve various aspects of internal combustion engines using these coatings. Thakare et al. (2021) conducted a review on Thermal Barrier Coatings (TBCs) highlighting their significant progress since initial development. TBCs are widely used in various engineering applications, including internal combustion engines, gas turbines, and pyrochemical units. Ongoing efforts aim to enhance substrate life by improving coating performance, making TBCs crucial for addressing long-term and short-term challenges in the industry. This review offers insights into thermal spray techniques, material advancements, mechanical properties, high-temperature performance, residual stress, failure mechanisms, and life prediction models for TBCs [1]. Ren et al. (2020) conducted research on multicomponent high-entropy zirconates, aiming to enhance thermal barrier coatings. Traditional ceramics face challenges due to brittleness and low thermal expansion. Entropy engineering creates new ceramics with substantial thermal expansion, great mechanical properties, and minimal thermal conductivity. This work introduces innovative ceramics for thermal barrier coatings and thermoelectric applications [2]. Li conducted research on creating High-entropy pyrochlores with low thermal conductivity for thermal barrier coatings. Using a solid-state reaction method, rare-earth zirconate-based high-entropy pyrochlore structures were successfully produced from a mix of rare-earth oxides (La_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, and Y_2O_3) and ZrO_2. The resulting $(5RE1/5)2Zr_2O_7$ high-entropy ceramics displayed exceptional sintering resistance, thermal stability, and thermal conductivity below 1 Wm–1K–1 from 300 to 1200°C, making them promising materials for thermal barrier coatings [3].

Iqbal & Moskal 2023 conducted research to understand the recent advances in ceramic materials and the mechanisms of degradation in thermal barrier coatings. High-temperature behavior of metallic alloys, including corrosion and protective layer formation, has been a long-standing scientific focus. Despite some alloys having an initiation period before hot corrosion progresses, no alloy combination remains impervious indefinitely. While nickel-based materials excel in harsh conditions, they often fall short of modern high-temperature demands. The research offers valuable insights for the development of resilient ceramics and effective protective coatings, crucial for high-temperature applications [4]. Iqbal et al. (1991) conducted research on recent advancements in ceramic materials and understanding the degradation mechanisms of thermal barrier coatings. It investigates hot corrosion behavior, advanced ceramics, and strategies for mitigation [5]. Rabiei & Evans (2000) conducted research investigating the failure mechanisms related to thermally grown oxide in plasma-sprayed thermal barrier coatings (TBCs). It explores the microstructure and durability of TBCs and their failure under different conditions [6]. Dutton et al. (2000) conducting research exploring the impact of heat treatment on the thermal conductivity of plasma-sprayed Y_2O_3 stabilized ZrO_2 (YSZ) and Al_2O_3 coatings. Heat treatment at 1300 °C in flowing argon for 50 hours significantly enhanced thermal conductivity due to microcrack sintering at splat interfaces, particularly in YSZ coatings. The observed increase was explained using a model for thermal conductivity in materials containing oriented penny-shaped cracks [7].

For further improving the properties of thermal barrier coatings, nanoparticles are being used. A lot of researchers have used nanoparticles for improving the properties of thermal barrier coatings. Karthik et al. (2013) conducted research on producing Al_2O_3-stabilized tetragonal ZrO_2 nanoparticles for thermal barrier coatings. These nanoparticles, measuring 26 nm with a surface area of 59 m^2/g, were characterized and applied to mild steel specimens, providing effective thermal protection at 600°C [8]. Shaisundaram et al. (2020) investigated the impact of thermal barrier coatings with different dosing levels of cerium oxide nanoparticles in diesel engines. This study addressed stringent exhaust emissions regulations for internal combustion engines. The research showed notable enhancements in engine efficiency and reductions in emissions. Brake thermal efficiency increased by 2.1%, while brake-specific fuel consumption decreased by 3% compared to standard diesel mode in uncoated engines. There were significant reductions in nitrogen oxide, carbon monoxide, and hydrocarbon emissions as well [9]. Zhao et al. (2016) conducted research focusing on enhancing carbon fiber architecture by introducing ordered silica nanoparticles. They used poly(1,4-phenylene diisocyanate) to modify the carbon fiber surface, improving reactivity. Silica nanoparticles were chemically grafted to the surface, enhancing interfacial properties. This led to increased interfacial shear strength with epoxy resin. Additionally, a siliconborocarbonitride ceramic coating improved antioxidant and ablation properties at high temperatures [10]. Shanmugam et al. (2021) investigated the impact of Thermal Barrier Coating (TBC) in Citron peel oil biodiesel-powered CI engines with cerium oxide nanoparticles. Biodiesel, an eco-friendly alternative, was tested to reduce greenhouse gases. TBC with Zirconia-Stabilized Yttria and Ceria improved performance. Results showed increased Brake Thermal Efficiency for B20+15 ppm, 10.59% lower Specific Fuel Consumption with TBC, elevated Exhaust Gas Temperature, and reduced emissions of CO, CO_2, and NOx. Coating morphology remained consistent despite carbon deposits after 20 hours of engine operation [11]. Sivakandhan et al. (2022) conducted research on the impact of MnO_2 nanoparticles in a sardine oil methyl ester (SOME) operated engine with thermal barrier coating. Results demonstrated enhanced performance and reduced emissions, with 25 ppm MnO2 showing a 7.5% increase in Brake Thermal Efficiency, 9.2% higher rate of heat release, and 7.2% increased in-cylinder pressure, while decreasing nitrogen oxides, hydrocarbon, and CO by 11.5%, 42.5%, and 7.4%, respectively. This suggests the potential for improved engine performance and emissions reduction with 25 ppm MnO_2 in SOME [12].

On studying previous investigations, research on nanoparticles incorporated ceria-yttria stabilized zirconia as thermal barrier coating were not conducted. Hence, in this investigation, an attempt has been made to study the characteristics of CuO nanoparticles incorporated ceria-yttria stabilized zirconia.

2. Materials & Methods

In this investigation, ceria-yttria stabilized zirconia in micropowder form and CuO nanopowder was purchased from Sigma Aldrich Chemicals Private Limited, Bangalore. As both the chemicals were of 99.9% purity, it was directly used in the experiments without further purification. Al piston material was used as the substrate over which the coatings were done. , Ceria-yttria stabilized zirconia was mixed with CuO nanopowder at different substitution ratios such. At 0.25% CuO, 0.5% CuO, 0.75% CuO and 1% CuO substitution, the combinations were prepared. The properties of ceria-yttria stabilized zirconia and CuO nanopowder is shown in Table 1. The abbreviations for nanoparticle with thermal barrier coating combination are shown in Table 2.

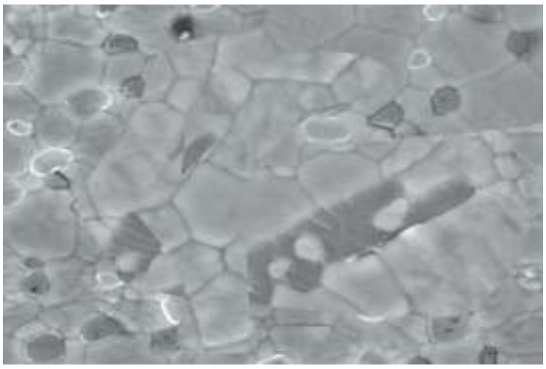
Table 1 – Properties of the base materials

Elements	Density (g/cc)	Hardness (Mohs)	Thermal conductivity (W/mK)	Compressive strength (MPa)	Modulus of elasticity (GPa)
Ceria-yttria stabilized zirconia	6.85	8	2.61	2368	203
CuO nanopowder	5.32	7.6	2.93	1985	169

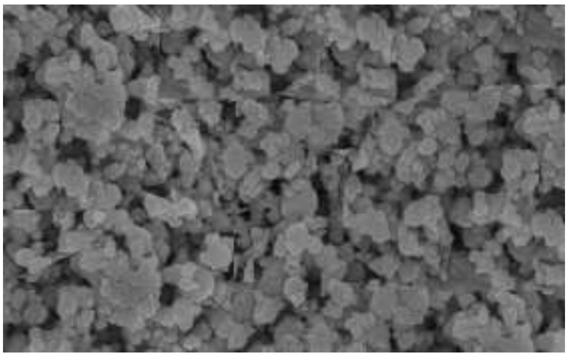
Table 2 – Combination of ceria-yttria stabilized zirconia with CuO nanopowder

S No	CuO nanopowder	Ceria-yttria stabilized zirconia	Abberevation
01	0.25%	99.75%	0.25TBC
02	0.5%	99.5%	0.5TBC
03	0.75%	99.25%	0.75TBC
04	1%	99%	1TBC

The SEM image of as received Ceria-yttria stabilized zirconia and CuO nanopowder are shown in Fig1 (a) and Fig1 (b).



(a)



(b)

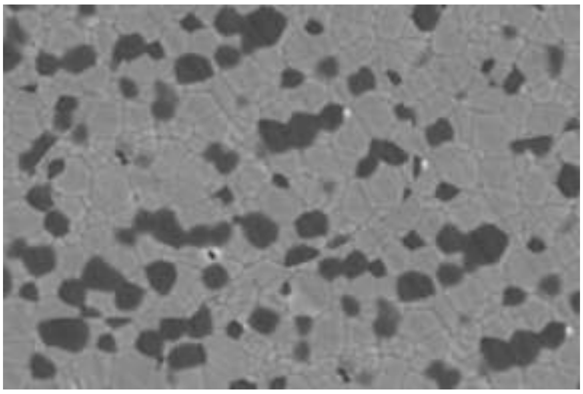
Fig1 (a) SEM image of as received Ceria-yttria stabilized zirconia, (b) SEM image of as received CuO nanopowder

From Fig1 (a), SEM image of Ceria-yttria stabilized zirconia exhibits a cubic fluorite structure. The presence and distribution of CeO2 and Y2O3 within the zirconia lattice can be observed. From Fig1 (b), SEM image of CuO nanoparticles exhibit spherical, rod-like structure. Tenorite crystal structure was found to be in abundance. Coating on the Al piston material was done using High velocity oxy fuel thermal spraying technique. Before coating, the aluminum substrate was prepared by cleaning and roughening the surface. This step is crucial for promoting adhesion between the coating and the substrate. The CuO nanoparticle-incorporated CeO_2-Y_2O_3-ZrO_2 powder is prepared. This composite powder typically consists of CuO nanoparticles homogeneously distributed within the CeO_2-Y_2O_3-ZrO_2 matrix. In the HVOF thermal spraying process, a mixture of oxygen and a fuel gas (LPG) is combusted in a torch to generate a high-velocity and high-temperature flame. The powder feedstock is injected into the flame, where it rapidly melts and accelerates. The high velocity of the particles and the intense heat ensures that the coating material adheres well to the substrate.

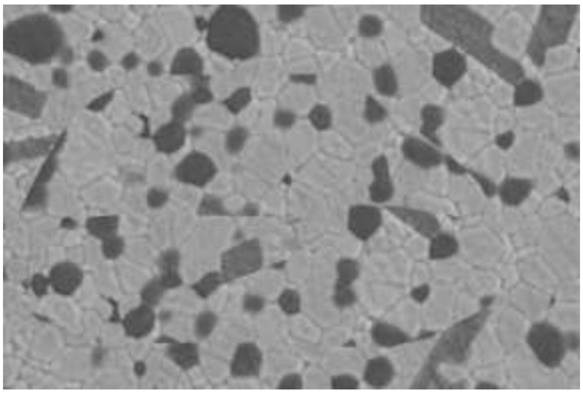
The molten CuO nanoparticle-incorporated CeO_2-Y_2O_3-ZrO_2 particles were sprayed onto the prepared aluminum substrate. The high kinetic energy of the particles promoted their bonding with the substrate, forming a dense, well-adhered coating. As the sprayed particles impact the substrate, they cool and solidify rapidly, forming a solid coating. The high velocity of the particles minimizes the heat transfer to the substrate, reducing the risk of substrate overheating. The microstructure aspects of the deposited coating can be characterized using Field Emission Scanning Electron Microscopy.

3. Results & Discussions

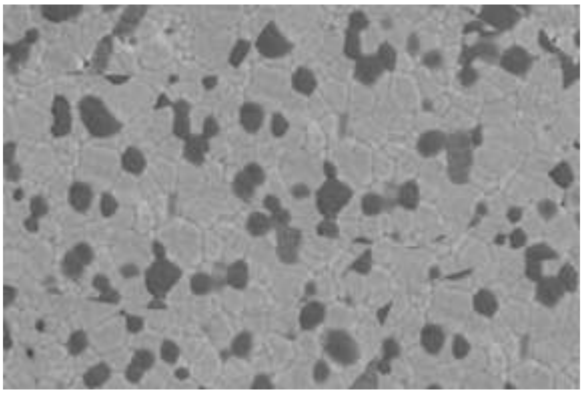
High resolution FE-SEM image of the coated surfaces are shown in Fig2. The FE-SEM image of 0.25TBC, 0.5TBC, 0.75TBC, 1TBC are shown in Fig2 (a), (b), (c) and (d) respectively.



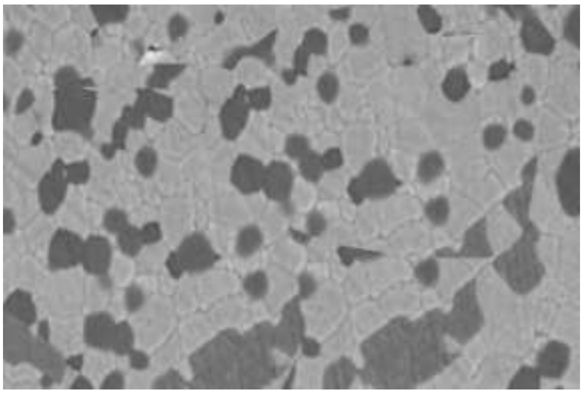
(a)



(b)



(c)



(d)

Fig2. FE-SEM images of (a) 0.25TBC, (b) 0.5TBC, (c) 0.75TBC, (d)1TBC

FE-SEM image of 0.25TBC indicated a reduction in the average grain size of the CeO_2-Y_2O_3-ZrO_2 grains. Smaller grains can increase the material strength. FE-SEM image of 0.5TBC indicated a change in the grain boundary structure due to the presence of CuO nanoparticles can affect the grain boundary structure. FE-SEM image of 0.75TBC indicated the stability of the cubic fluorite structure of CeO_2-Y_2O_3-ZrO_2. This can lead to phase transformations and alter the mechanical and ionic conductivity properties of the material. FE-SEM image of 1TBC indicated defects such as oxygen vacancies and interstitials. These defects can influence ionic and electronic conductivity, catalytic activity, and oxygen storage capacity in the material. This interaction may lead to the formation of solid solutions or other compound phases, potentially altering the material's properties, including its electronic and ionic conductivity. The addition of CuO nanoparticles may affect the distribution and dispersion of dopants (e.g., cerium, yttrium, and zirconium) within the composite. This can influence the stability of the cubic phase and the material's ionic conductivity. The presence of CuO nanoparticles can alter the dislocation density in the material. Changes in dislocation density affect mechanical properties like hardness, fracture toughness, and deformation behaviour.

4. Conclusions

In this investigation, an attempt has been made to investigate the effects of incorporating CuO nanoparticles into ceria-yttria stabilized zirconia (CeO_2-Y_2O_3-ZrO_2) for use as thermal barrier coatings. Changes in grain structure were examined by varying CuO nanoparticle content from 0.25% to 0.75% by weight and the following conclusions were made.

(i). The study revealed significant microstructural modifications as CuO nanoparticles were incorporated into the CeO_2-Y_2O_3-ZrO_2 matrix. These modifications included changes in grain size, grain boundary structure, and crystal stability.

(ii). The addition of CuO nanoparticles led to a reduction in the average grain size of CeO_2-Y_2O_3-ZrO_2. Smaller grains can contribute to improved material strength, which is essential for thermal barrier coatings.

(iii). The presence of CuO nanoparticles induced changes in the grain boundary structure, which can impact mechanical and thermal properties. These alterations are important for understanding the behavior of the coating under thermal stress.

(iv). Stability of the cubic fluorite structure in CeO_2-Y_2O_3-ZrO_2 was confirmed, which is essential for its application in thermal barrier coatings. Maintaining this structure is crucial for its performance.

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