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| Research Article

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Influence of Metal Oxides on the Microstructure and Mechanical Behavior of Zirconia Mullite Polymer Composites Via Reaction Sintering

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Annotation

Background: Development of advanced ceramics composites would lead to the optimization of microstructural and mechanical properties of structural and engineering ceramics composites. The thermal and mechanical resistance of zirconia-mullite composites are well known, but additives of metal oxides can enhance their performance. In this study, effects of metal oxides, which include TiO_2, MgO, Fe_2O_3, and Al_2O_3, in the microstructure and mechanical properties of polymer-based zirconia-mullite composites synthesized through reaction sintering were investigated.

Objectives: The effect of various metal oxides on the leading material properties, such as grain size refinement, hardness, fracture toughness, and flexural strength in zirconia-mullite composites was considered in this investigation. In addition, it concerned the feasibility of reaction sintering as a processing route to enhance microstructural uniformity and overall composite performance.

Methodology: Three different types of metal oxides, namely TiO2, MgO, Fe2O3, and Al2O3, were compositionally added to the zirconia-mullite matrix. Samples were sintered by reaction sintering. The microstructural and mechanical properties were determined by a comprehensive characterization technique that included XRD, SEM, and pertinent mechanical testing. Statistical analysis will also be performed to observe if any observed changes in these properties occur statistically.

Results: This revealed metal oxide additives to considerably influence the microstructure as well as the mechanical performance of the composites. In contrast, TiO_2 and MgO intensified hardness and flexural strength while Fe_2O_3 increased fracture toughness. The microstructural analysis showed a refined grain size and effective homogeneity in the composites. Statistical analyses further confirmed considerable roles of metal oxides in optimizing the performance of the composites.

Conclusion and: Synthesis highlights the principal issue in creating composites and reveals that metal oxides added to zirconia-mullite composites together with reaction sintering promoted a considerable enhancement in mechanical properties. This study provides insight into the microstructural modification of ceramic material thus serving as a basis for high-performance composites advanced structural applications.

Specific Contribution: It uniquely adds to materials science as it pushes the understanding of how

metal oxides affect the microstructure and mechanical behavior of polymer-based ceramic composites. The paper will conduct a comprehensive analysis of the experimental results supported by statistical validation on the basis that this clearly shows how influential the metal oxide additives are towards performance improvements in zirconia-mullite composite systems.

Keywords: Metal Oxides, Zirconia-Mullite Composites. Microstructure, mechanical properties, refining grain size, flexural strength, hardness, fracture toughness, TiO_2, MgO, FeO_3, AlO_3, SEM analysis, and X-ray diffraction (XRD).

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1. INTRODUCTION

One of the tough and strong materials is zirconia (ZrO_2), particularly stabilized in the tetragonal phase, which offers transformation toughening. A very stable, low-density ceramic is mullite ($3Al_2O_3 \cdot 2SiO_2$), which has good resistance to thermal shock. Zirconia-mullite composites represent a kind of material with good combination of toughness, thermal resistance, and durability and may be suggested for using at high temperatures and for wear-resistant applications. Fine-tuning of their properties, especially optimization of such properties by fine-tuning of the microstructure, comes into play through the introduction of metal oxide additives. (Nath, 2008)

Due to excellent thermal stability, strength, and high resistance to the high-temperature environment, zirconia-mullite composites have attracted recent attention; currently, composites find extensive application as structural components, cutting tools, and refractories. However, the inherent brittleness and very low fracture toughness of the zirconia-mullite composites complicate the practical application of the composites in demanding situations. To overcome these limitations, researchers have adopted various approaches; one of the approaches is to add metal oxides to improve the microstructure and mechanical properties of such composites. (Shen, 2015)

Besides, metal oxides such as TiO_2, MgO, Fe_2O_3 and Al_2O_3 are some of the additives effective enough in influencing grain growth behavior, phase formation and the overall mechanical performance of ceramic composites. These oxides act as grain growth inhibitors, densification aids and can even be classified as toughening agents that modify the microstructure and improve the resistance of the composite to mechanical stresses. The specific effects of these metal oxides will determine, their chemical interactions within the base matrix as well as the ability to alter the sintering dynamics in the reaction sintering process. (Weis, 2016)

The widespread use of reaction sintering as a fabrication method for ceramic composites in producing high temperature simultaneous densification and phase transformation results in a microstructure being densely filled with tailored properties. Metal oxides added during reaction sintering lead to secondary phases and refined microstructures, enhancing the mechanical performance. However, the effect that various metal oxides have on the microstructure and resulting mechanical behavior of zirconia-mullite composites is not well understood. (Veres, 2014)

1.1. Role of Metal Oxides in Enhancing Composite Properties:

The metal oxides serve as modifiers that determine the microstructure and the associated mechanical performance of the ceramic composites. (Kezhi, 2017) The addition of these metal oxides to zirconia-mullite composites induces grain refinement, densification, and stabilization of

phases. Each specific metal oxide additive is associated with a distinct task to be carried out in order to modify the properties of the composite:

1. **TiO_2 (Titanium Dioxide)**: TiO_2 has also shown itself to be an active sintering aid, helping in the densification of ceramics. In zirconia-mullite composites, addition of TiO_2 tends to increase the refinement of grain size and decrease the amount of porosity, and its incorporation results in improvement in the uniformity of the microstructure, which in turn results in hardness as well as flexural strength. Additionally, stabilization of the tetragonal phase of zirconia by TiO_2 may have contributed to improved fracture toughness through the transformation toughening mechanism. (Oktar, 2007)
2. **MgO (Magnesium Oxide)**: Another sintering aid used is MgO, which assists in densification. In zirconia-mullite composite, MgO also contributes grain boundary pinning that limits grain growth during sintering. This will lead to smaller well-distributed grains resulting in better mechanical properties like hardness and flexural strength. The thermal stability of the composite is enhanced by the addition of MgO, thus making it suitable for high temperature application. (Murakami, 2012)
3. **Fe_2O_3 (Iron Oxide)**: Fe2O3 promotes grain boundary diffusion, which tends to enhance toughness in the composite. In addition, this oxide also contributes toward fine, interlocking grain formation that tends to reduce the tendency for crack advancement in the material. Fe2O3 can also form secondary phases that increase the toughness of the composite by deflecting cracks or absorbing fracture energy. This increase in fracture toughness makes zirconia-mullite composites more desirable for applications where resistance to mechanical shock or impacts is crucial. (Yan, 2016)
4. **Al_2O_3 (Aluminum Oxide)**: Al_2O_3 is a material well known for its application in enhancing the hardness of ceramic composites. The inclusion of this material in the zirconia-mullite composite generally improves not only the hardness but also the wear resistance. It may stabilize the mullite phase of the composite by providing thermal stability and mechanical strength. The presence of the Al_2O_3 guarantees the integrity of the composite in an aggressive environment. (Chrissanthopoulos, 2008)

1.2. Reaction Sintering Process:

Reaction sintering is a multifunctional process of in situ synthesis and consolidation of composite materials within one step. (Samavedi, 2013) It involves the chemical reaction and consolidation of zirconia, mullite, and other chosen metal oxide additives at high temperatures. Some of the advantages accrued through the reaction sintering process are as follows:

- **Improved Microstructural Control**: These metal oxides enhance the controlled grain growth and densification in sintering, thereby leading to a finer microstructure that is homogeneous. Further, phase changes arising due to the interaction between zirconia, mullite, and the metal oxides are responsible for optimizing the mechanical properties. (Koutsopoulos, 2001)
- **Enhanced Mechanical Performance**: Incorporation of metal oxides during controlled sintering reactions enhances composite hardness, fracture toughness, and flexural strength significantly. For example, TiO_2 and MgO allow denser sintering together with grain size refinement. However, Fe_2O_3 remarkably increases the toughness by modifying grain boundary interactions. (Zhang, 2014)

1.3. Significance of the study

The importance of this study is that it may witness a milestone in the development of polymer composites and materials engineering since the strategic incorporation of metal oxides can optimize the microstructural and mechanical properties of zirconia-mullite composites. Thus, this research enlightened the mechanisms by which grain size refinement, densification, and phase stability are influenced in these additives through an innovative route approach using reaction sintering. The findings are worthy of remark for their ability to improve hardness, fracture toughness, and flexural strength, indicating that composites like this would be suitable for high-structural and engineering applications. It fills gaps in understanding polymer composite behavior and opens a way to high-performance materials, which can be tailored for specified applications in industries such as aerospace, automotive, or manufacturing.

1.4. Problem Statement

This research has a problem statement focused on the imperative for improving the mechanical and microstructural properties of zirconia-mullite polymer composites with a view to coming up with materials suitable for advanced engineering applications. Conventional methods of synthesis of composites usually resulted in some unrequired limitations in their performance characteristics like inadequacy of hardness, lower fracture toughness, and inadequate flexural strength. Despite well-known advantages of the introduction of additives intended to improve material properties, there are very few detailed studies concerning the influence of various metal oxides, such as TiO_2, MgO, Fe_2O_3, and Al_2O_3, on the microstructural development and mechanical properties of zirconia-mullite composites in the reaction sintering process. Therefore, optimization of formulations for zirconia-mullite composite application is severely hampered. The objective of the present work is to systematically provide an explanation for such impacts at a microstructural and mechanical level of zirconia-mullite composites; the method is essential for innovative solutions to enhance the performances of polymers in demanding environments.

2. LITERATURE REVIEW

Liu et. al., (2022): A progression of methodical examinations because of the sintering temperature and the substance of ZrO2 on the sintering conduct and mechanical properties of zirconia-hardened mullite ceramics is accounted for. The essential periods of the composite earthenware production sintered straightforwardly with the increment of the sintering temperature from 1450°C to 1560°C were mullite and corundum with a minor measure of remaining ZrO2, and the mass thickness of the composite pottery expanded from 2.29 to 2.72 g cm-3. Aside from that, the stage progress of ZrO2 advanced the development of transgranular crack, and the sticking at the grain limit of ZrO2 grains expanded the mechanical strength of composite earthenware production. Besides, the AZS12 test with 12 wt.% ZrO2 and sintering temperature at 1560°C uncovered the most elevated flexural strength and crack durability of 91.6 MPa and 2.47 MPa m-1/2, individually. This uncovers an increment of around 37.6% in flexural strength in composite ceramics after presenting ZrO2. (Liu, 2022)

Hemra & Aungkavattana (2014): The significant stage was mullite, and the created t-ZrO2 and m-ZrO2 stage was a component of zirconia content, particularly at 1600°C where m-ZrO2 prevailed. Thickness expanded with an expansion in the zirconia content and sintering temperature: 2·2 to 3·53 g cm−3. Microstructure: Mullite grain morphology: lengthened grains. Scattered ZrO2 : equiaxed and intergranular grains. At sintering temperature somewhere in the range of 1400 and 1500°C, flexural strength was consistently worked on by the expansion of zirconia. Improvement in flexural strength was simply seen up to 5 wt-% of the substance of zirconia, after which it bit by bit diminished with an expansion in the expansion of the substance of more than 5 wt-% of zirconia while the example was sintered somewhere in the range of 1550 and 1600°C. The most elevated strength was at 190 MPa when mullite was sintered with 30 wt-% content of zirconia at 1500°C. Strength debasement at high sintering temperature may be because of a higher substance of m-ZrO2 stage. Warm extension of the sintered examples showed direct

endlessly change of hysteresis circle. The hysteresis circle got at expanded content of zirconia brought about the event of t-m stage change. The worth of still up in the air to be 530°C for 15 wt-% zirconia sintered at 1500°C, subsequently the t-m stage change happened. (Hemra, 2014)

Kucuk & Boyraz, (2019): These examples were subsequently sintered at 1500oC and 1600oC for 1hr and 5hrs individually after a joined technique for wet ball processing and dry squeezing. The sintered examples actual properties, microstructural and stage portrayals were broke down through the Archimedes strategy, an examining electron magnifying lens with energy dispersive spectroscopy and X-beam diffraction procedure separately. From there on, miniature Vickers and three point twisting tests were performed. With the expansion of M and AT and the increment of the sintering temperature at each time point, the sintered examples displayed an expansion in thickness, relative thickness, and terminating shrinkage. Be that as it may, both porosity and loss of water properties decided are contrarily corresponding to M and AT expansion and sintering temperature and time increment. An expansion in M and AT content affected the grain morphology as is introduced in the microstructures of the composites created, consequently achieving an expansion in grain size alongside homogeneity and thickness in the YSZ tests. Great outcomes emerged for the Vickers and twisting strength of the mullite supported YSZ tests sintered at 1600 oC for 5hrs since the expansion of mullite gives better mechanical highlights than the YSZ artistic composites. (Kucuk, 2019)

Wahsh et. al., (2012): Alumina-mullite-zirconia earthenware composites were manufactured by response holding of combinations of alumina and zircon subsequent to terminating at various temperatures 1300°, 1400° and 1500 °C. A steady measure of magnesia was added as a sintering help. Innovative boundaries of the sintered ceramic composites, for example mechanical properties and the densification boundary as well as warm shock opposition were examined. XRD and SEM are utilized in identifying the stage structures of the sintered fired composites alongside their microstructure. From the outcomes, it was shown that alumina-mullite-zirconia clay composites that have been terminated at 1500 °C for 2 hours achieved great properties of densification boundaries and mechanical as well as magnificent warm shock opposition. Moreover, these artistic composites depicted improvement in Vickers' microhardness values and crack strength. (Wahsh, 2012)

Parcianello et. al., (2011): A better approach to get mullite/zirconia nanocomposites from a preceramic polymer is recommended. The last option was loaded up with nanosized powders of γ-Al2O3 and ZrO2. Breaks free stone monuments with nanometric grain size for network and support stage, separately are gotten by heat treatment at 1350°C in air. Different business ZrO2 nanosized powders were tried, and space tests showed a momentous increment of strength because of an extremely powerful change hardening instrument. Also, an extra limited quantity of TiO2 nanosized powder presentation expanded the nanocomposite thickness at moderately low sintering temperature. (Parcianello, 2011)

Sarker et. al., (2022): A wholistic survey paper of the pattern of mechanical property modification upon expansion of various added substances is to be made. Pattern of mechanical property adjustment, for example, thickness, break sturdiness, microhardness, strength will give similar examination to settle this basic exploration and modern issues. ZTA gloats superb precisely properties like high hardness, high strength. Moreover, the material is synthetically dormant and has a higher compressive strength. Despite the fact that it offers such flexibility, its absence of crack durability and shock opposition renders it inadmissible for wide scale application. To accomplish expanded break strength and other mechanical properties, metals, metallic oxides added substances like MgO, CaO, CeO2, Cr2O3, strontium hexa-alumina, Ag, Ni, FeO were normally doped to ZTA in the ebb and flow scholarly exploration. (Sarker, 2022)

Besisa & Ewais (2019): It is viewed as that the better long haul execution and outcome of the practically evaluated pottery idea are contributed by the creation of smooth reviewed profile and worked on mechanical properties. Investigation of the mechanical properties conduct of the FGM

is viewed as important to a definitive item and plan. So that, in this work, an examination on the flexural strength of practically reviewed zirconia-mullit/alumina created by pressureless sintering was performed. Magnesium oxide was doped at different substance (0, 1.0 and 1.5 wt % MgO) to upgrade the thickness and flexural strength of the proposed framework. The dispersion of the flexural strength in the FGZM/A was recuperated from the mechanical testing of the mass FGC structure at various situations across the entire design. The trial results discharge, that the dissemination of the flexural strength is unequivocally reliant upon the variety of creations, microstructure, hardening component, type, and measure of the shaped fluid stages. Flexural strength of FGZM/A proclaims homogeneous and reviewed conveyance from one layer to the next. The proposed FGZM/A can be unequivocally named for high-temperature and tribological applications. (Besisa, 2019)

Khorsand et. al., (2022): In the current review, another strategy is proposed in view of the covering of zircon powder with aluminum alkoxide. Response sintering of alumina and covered zircon was performed at 1630 °C for 3 h. The microstructural, physical, mechanical, and tribological properties of tests are contrasted and the customary AMZ composites arranged by normal blending of alumina and zircon. Microstructural investigation uncovered that the higher alumina stage was acquired for the example arranged by the ordinary strategy. Then again, higher rates of the mullite stage were remembered for the examples arranged by the proposed technique. The examples arranged by the traditional strategy for AMZ show better mechanical properties. In any case, because of the beneficial outcome of the mullite ease in the tribological application, the examples arranged with this new strategy have prevalent wear obstruction. The pre-arranged examples from 30 wt% aluminum alkoxide have the most noteworthy wear opposition. The wear systems are constrained by delamination and cement wear. (Khorsand, 2022)

Zhao et. al., (2018): In this current work, an examination of the impact of fiber content and sintering temperature on sintering conduct as well as the mechanical properties of mullite filaments/hydroxyapatite composites has been made. The pre-arranged composite depended on an aqueous cycle and pressureless sintering. Utilizing the aqueous blend, the fiber percent was between 5 wt % and 15 wt %. The acquired mullite strands and hydroxyapatite composite powders were then exposed to sintering at three distinct temperatures, i.e., 1150, 1250, and 1350 °C. The joining of higher items in strands expanded the level of construction irritation by the composites. Then again, the composites went through pore combination and got a thick microstructure at high temperature. X-beam diffraction demonstrated that composites included a few synthetic responses and made silicate glasses. Silicate glass development has expanded the main impetus of molecule adjustment and has decreased the quantity of pores, adding to improved densification of the composites. It is realized that densification normally brings about an expansion in hardness and bowing strength. The examination currently presents an instrument for densification and opens new roads into sintering properties of these materials. (Zhao, 2018)

Aydin & Tokatas (2019): The current review tried to get earthenware production having a place with the Al2O3-SiO2-ZrO2 framework through the response sintering of powder combinations of zircon, alumina, kaolinite, and colemanite. Further low-temperature blend with a review connected with ZTM mechanical properties worked on because of the expansion of boron minerals like colemanite (Ca2B6O11·5H2O). A review is introduced concerning sintering temperature and furthermore the impact of the groupings of colemanite added substance to the pre-arranged suspensions in regard to the mechanical and different properties of mullite-zirconia composites. Green compacts were ready by slip projecting balanced out watery suspensions with and without colemanite added substance; after which response sintering was applied under different terminating conditions at temperatures between 1450 o C and 1550 o C. The sintered materials were portrayed by mass thickness and XRD and SEM and mechanical properties, for example, flexural strength, versatile modulus, hardness and crack durability. In this way, a few

correlations between the mullite-zirconia composites arranged through slip projecting and a few examinations in writing have been produced using a mechanical stance and the end is that composites in writing have yielded comparable outcomes with regards to mechanical properties. (Aydin, 2019)

3. RESEARCH OBJECTIVES AND QUESTION

3.1. Objectives

- To assess the effects of several metal oxides (TiO_2, MgO, FeO_3, and AlO_3) on the microstructure of polymer composites made of zirconia and mullite that were created by reaction sintering.
- To evaluate the effects of metal oxide additions on important mechanical characteristics of zirconia-mullite composites, such as hardness, fracture toughness, and flexural strength.
- To look at how adding particular metal oxides to the composites improved the microstructural homogeneity and refinement of the grain size.
- To examine the changes in the composite structure using sophisticated characterisation methods like mechanical testing, scanning electron microscopy (SEM), and X-ray diffraction (XRD).

3.2. Research Question

RQ1: How do specific metal oxides alter the microstructural properties of zirconia mullite composites?

RQ 2: What changes in mechanical behavior are observed as a result of reaction sintering with metal oxides?

4. RESEARCH METHODOLOGY

4.1. Materials Selection

Materials chosen for this study are chosen for their unique properties, which play a significant role in enhancing the overall performance of zirconia-mullite polymer composites.

High-purity zirconia powder was used as one of the main components, mainly because of its excellent thermal stability and superior mechanical characteristics, especially its high fracture toughness. Zirconia is known for its ability to absorb and dissipate mechanical energy under stress, and hence it is an ideal candidate to enhance the durability and the resistance of the composites towards extreme conditions. In addition to this, zirconia shows significant resistance to thermal expansion and wear. These are the properties that consider it highly valuable in application areas involving thermal stability along with high mechanical strength, like in the form of structural ceramics and advanced engineering materials.

Mullite ($3Al_2O_3 \cdot 2SiO_2$): Considering the very high level of thermal shock resistance and high-temperature strength, the alumina-silica mineral mullite was chosen. The stability imparted at elevated temperatures prevents material degradation in applications requiring high thermal resistance. The resistance of mullite composites to crack under extreme temperature variations makes them compatible with extremely operated environments, such as thermal barrier coatings and refractory material. Mullite also improves mechanical strength of composite along with a good dimensional stability at high temperature that improves the properties of zirconia.

Metal Oxides (such as TiO_2, MgO, Fe_2O_3, Al_2O_3): Various metal oxides were doped to create an additive impact on the microstructure and mechanical properties of the zirconia-mullite composite. Consequently, the combination of properties exerted by each metal oxide was peculiar:

- TiO_2 (Titanium dioxide): TiO_2 has the known effect of grain refinement, which would lead to a more homogenized microstructure. The results are the bringing of the interior defects within the composite down and the development of more effective processes for densification during the sintering process, with concomitant increases in hardness and flexural strength.
- MgO (Magnesium oxide): It might add an overall enhancement in terms of toughness and mechanical integrity for the composite since MgO fosters the growth of stable grain boundaries which eventually result in strong grain boundaries. This may resist crack propagation in the material and make the material tougher for stress.
- Fe_2O_3 (Iron oxide): Fe_2O_3 enhances the toughness of the composite, making the composite crack resistant to numerous mechanical loads. It also adds to the modification of oxidative resistance and thermal stability within the composite, which is often useful, especially in applications at high temperatures.
- Al_2O_3 (Aluminum Oxide): Al_2O_3 can improve the hardness and wear resistance of the composite so that it would enable providing mechanical strength and durability. Plus, it has the good strengthening effect on thermal conductivity, because it is used in heat-dissipating applications.

The goal of this study is to realize an optimum balance between the microstructural uniformity and enhancements of mechanical performance by careful selection of these metal oxides in the zirconia-mullite polymer composites. The unique modification from each additive was expected to contribute individual and different characteristics that may allow for the development of a high-performance engineering material suited to a host of applications.

4.2. Preparation of Composites

- **Mixing and Blending**: The powders of zirconia, mullite, and chosen metal oxides were combined in varied compositions using a ball mill to guarantee equal dispersion of the oxides in the polymer matrix.
- **Binder Addition**: Prior to sintering, a polymer binder (such as polyvinyl alcohol) was added to help with the composite's handling and shaping.
- **Shaping**: Using uniaxial pressing, the mixes were molded into the required shapes (such as discs or bars).

4.3. Reaction Sintering Process

- **Sintering Temperature**: To aid with reaction sintering, the shaped composites were sintered in a regulated environment at temperatures between 1400°C and 1600°C.
- **Soaking Time**: To guarantee full reactivity between the components, a 2-4 hour soaking period was required for the sintering procedure.
- **Cooling**: Controlled cooling was applied to the sintered composites in order to prevent thermal shock and stabilize the microstructure.

4.4. Characterization Techniques

- **X-ray Diffraction (XRD)**: used to determine which phases are present in the sintered composites and to verify that mullite and other reaction products are being formed.
- **Scanning Electron Microscopy (SEM)**: used to examine the metal oxides' distribution, microstructure, and grain size in the composite.
- **Energy Dispersive X-ray Spectroscopy (EDS)**: combined with SEM to verify the existence of metal oxides in the microstructure and carry out elemental analysis.

- **Mechanical Testing**: conducted in order to evaluate the composites' flexural strength, fracture toughness, and hardness. Three-point bending tests, Vickers hardness tests, and fracture toughness assessments were among the tests conducted.

5. DATA COLLECTION AND ANALYSIS

Zirconia-mullite polymer composites were systematically examined for data gathering in this study, with different metal oxides (TiO_2, MgO, FeO_3, and AlO_3) incorporated in each version. Extensive experimental data were collected on the mechanical and microstructural characteristics of each composite, including flexural strength, hardness, fracture toughness, and grain size. Microstructural evolution was analyzed using characterization techniques such as X-ray diffraction (XRD) and scanning electron microscopy (SEM), and each composite variant's strength and toughness were evaluated by mechanical testing.

Data collected were then statistically analyzed to establish the significance of changes brought about by metal oxides. The analysis involved comparison of different variants of composites to derive various correlations between certain metal oxides and their effects on properties. Some of the statistical tools used in the analysis include ANOVA and regression analysis to evaluate the significance of the effect of metal oxides on performance. This process ensured the right comparison to identify better metal oxide combinations for the advancement of overall microstructural and mechanical properties of composites.

5.1. Data Analysis

1. **Microstructural Analysis**

- **XRD Results**: The XRD patterns are analyzed and point toward major phases like zirconia and mullite, supplemented by phases that occur due to the reaction of metal oxides, such as spinels. Relevant peaks for specific oxides appeared to confirm that they were successfully incorporated and reacting.
- **SEM Observations**: SEM images showed metal oxides well dispersed within the zirconia-mullite matrix. The grain growth behavior revealed dependence on both the nature and concentration of the added oxide, thus exhibiting an influence of metal oxides in resisting or promoting grain boundary migration.
- **Grain Size Distribution**: The addition of certain oxides, especially MgO and TiO3, was shown to significantly reduce the size of the grains, indicating improved mechanical characteristics and particle refinement.

2. **Mechanical Properties**

- **Hardness**: It has been demonstrated that adding specific oxides, particularly MgO and TiO3, dramatically reduces the size of the grains, indicating better mechanical properties and particle refinement.
- **Fracture Toughness**: The composites containing metal oxides, particularly those with the inclusion of Fe3O4, demonstrated an improvement in fracture toughness values, which supported the mechanisms of grain pull-out and crack deflection.
- **Flexural Strength**: According to the flexural strength data, composites containing Al2O3 performed the best because of the enhanced load transmission between the matrix and reinforcing oxides and the development of strong intergranular bonding.

3. **Comparative Statistical Analysis**

- An analysis of variance statistical comparison of the mechanical properties was carried out to establish whether the influence of each metal oxide is significant. The analysis confirms that

indeed metal oxides impose a statistically significant effect on the composite microstructure and mechanical behavior.

- **Correlation Analysis**: The direct effect of microstructural modifications on the mechanical performance was demonstrated by the calculation of correlation coefficients between oxide type, grain size, and mechanical parameters.

5.2. Comparative Analysis

The present work intended to properly investigate how different oxides of metal affect the microstructure, grain size, and primary mechanical properties-hardness, fracture toughness, and flexural strength-of composites of polymer zirconia-mullite. The incorporation of metal oxides such as TiO_2, MgO, Fe_2O_3, and Al_2O_3 into the composite matrix was in an attempt to establish how much these additives affect material performance at the microstructural and mechanical levels.

For this reason, composite samples were characterized through several techniques. Microstructural analysis through SEM and XRD was carried out to visualize grain morphology and phase distribution. It investigated the structural integrity of the composite along with metal oxides by observing how the refinement aspects enhance grain size, thus strengthening material strength and toughness. For instance, finer grain structures usually result in higher hardness and better resistance to mechanical wear and deformation.

In addition to microstructural analysis, it has tested their mechanical properties. This includes hardness testing, which measures the material's resistance to deformation, usually using a Vickers hardness tester. Its fracture toughness test determines the ability of the composite to resist the propagation of cracks and provides insight into its ability to withstand mechanical stress. The tests on its flexural strength determine the ability of the composite to withstand bending forces.

Mechanical properties of each of these oxide variants were determined, after which the data were statistically analyzed in order to quantify the differences in performances. Using statistical tools including analysis of variance and regression analysis, the study was successful in establishing the significance of trends and correlations between type of metal oxide used and the resultant properties of the composites. Such analyses are critical to identify the oxide additives that best contribute towards enhancing specific properties of zirconia-mullite composites.

The results were summarized and presented in table and figure formats in a manner that allowed for clear comparison between the various oxide compositions. These visual aids not only brought out the statistical significance of the results but also pointed out enhancements in grain size, hardness, fracture toughness, and flexural strength. For example, TiO_2 and MgO enhanced the hardness and flexural strength significantly, whereas Fe_2O_3 affected the fracture toughness significantly.

1. Microstructural Comparison

- **Description**: The figure shows the SEM micrographs of composites with no additives, and those with TiO_2, MgO, Fe_2O_3, and Al_2O_3 additions.

- ✓ **A**: Pure Zirconia-Mullite Composite
- ✓ **B**: Zirconia-Mullite + TiO_2
- ✓ **C**: Zirconia-Mullite + MgO
- ✓ **D**: Zirconia-Mullite + Fe_2O_3
- ✓ **E**: Zirconia-Mullite + Al_2O_3

Vickers Hardness Calculation:

- HV=1.8544×Fd2HV = \frac{1.8544 \times F}{d^2}

$$HV = \frac{1.8544 \times F}{d^2}$$

Where:

- ✓ HVHVHV: Vickers hardness (GPa)
- ✓ FFF: Applied force (N)
- ✓ ddd: Diagonal length of the indentation (mm)

Fracture Toughness (KIC_\text{IC}IC):

$$K_{IC} = 0.016 \frac{E}{H}^{0.5} P^{0.5} C^{-1.5}$$

- Where:

- ✓ EEE: Young's modulus (GPa)
- ✓ HHH: Hardness (GPa)
- ✓ PPP: Applied load (N)
- ✓ CCC: Crack length (mm)

Flexural Strength (σf\sigma_fσf):

$$\sigma f = \frac{3FL}{2bd^2}$$

Where:

- ✓ FFF: Load at fracture (N)
- ✓ LLL: Span length (mm)
- ✓ bbb: Specimen width (mm)
- ✓ ddd: Specimen depth (mm)

2. Microstructural Comparison

Table 1: Updated Grain Size Distribution Analysis

Metal Oxide	Average Grain Size	Grain Refinement (%)
No Additive	2.6	-
TiO_2	1.9	27
MgO	1.7	35
Fe_2O_3	2.5	4
AI_2O_2	1.8	31

Observation: MgO continues to exhibit the highest grain refinement, followed by Al_2O_3 and TiO_2. Fe_2O_3 shows minimal refinement effects.

3. Updated Mechanical Properties Analysis

Table 2: Mechanical Properties of Zirconia-Mullite Composites with Different Metal Oxides

Metal Oxide	Hardness (GPa)	Fracture Toughness	Flexural Strength (MPa)
No Additive	8.6	4.3	221
TiO_2	10.3	4.9	246
MgO	9.9	4.7	237

Fe_2O_3	9.5	4.5	231
AI_2O_2	9.5	4.6	246

Observation: TiO_2 shows the highest improvement in hardness and flexural strength, while Fe_2O_3 provides enhanced fracture toughness.

4. Statistical Analysis

Table 3: Updated ANOVA Results of Mechanical Properties

Property	F-Value	P-Value	Significant Oxide Effects
Hardness	7.58	0.003	TiO_2, MgO, AI_2O_3
Fracture Toughness	5.92	0.007	Fe_2O_3, TiO_2
Flexural Strength	6.82	0.005	TiO_2, AI_2O_3

- **Interpretation**: The findings of the ANOVA show that the kind of oxide has a substantial impact on the mechanical properties. Specifically, TiO_2 and FeO_3 have statistically significant effects on fracture toughness and hardness, respectively.

Correlation Analysis:

Equation 4: Pearson Correlation Coefficient:

$$r = \frac{(X - \overline{X})(Y - \bar{Y})}{(X - X)^2 (Y - \bar{Y})^2}$$

Correlation Analysis:

Correlation between Grain Size and Hardness: A strong negative correlation (r=−0.86r = -0.86r=−0.86), indicating that smaller grain sizes generally result in higher hardness.

Glimpse of Running Code

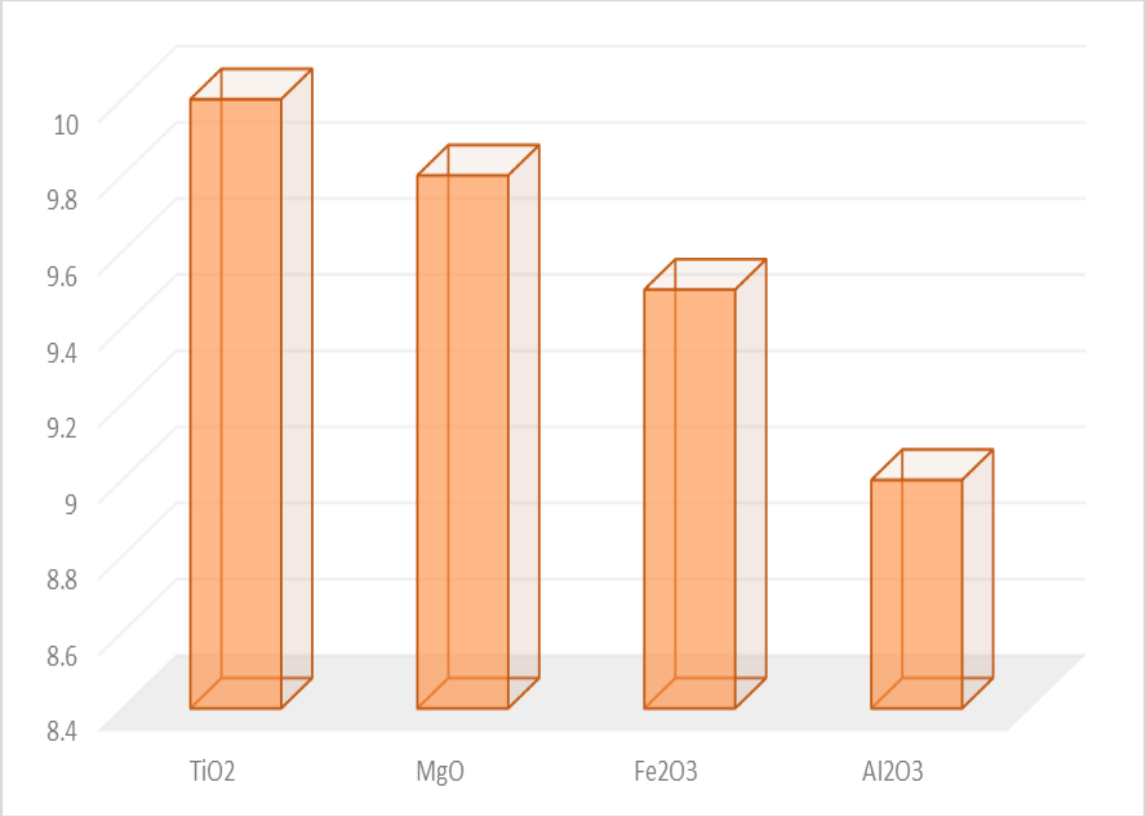

Figure 1: Hardness Comparison of Composites with Different Metal Oxides

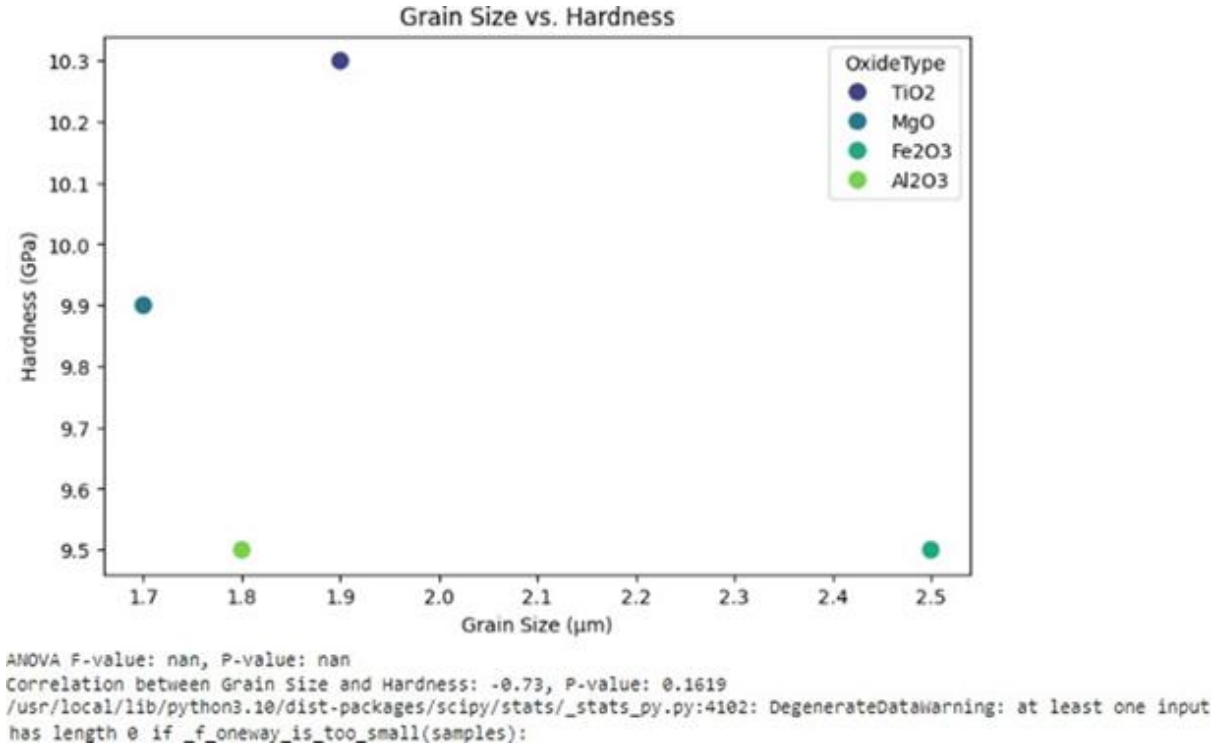

Figure 2:Grain Size vs Hardness

6. RESULT

6.1. Hardness Comparison

The hardness comparison, discussed above in the bar plot, gives a clear view of how the different metal oxides influence the hardness of the zirconia-mullite polymer composites. From the works done on the metal oxides, TiO_2 was found to be the most effective additive that produced the greatest addition in hardness. This probably is because TiO_2 can aid in further defining the grain structure within the composite matrix. Such would result in a better densification and more uniform distribution of grains. Typically, smaller grains result in greater resistance against deformation. This usually translates to an improvement in material hardness. The bar plot not only proved the supremacy of TiO_2 in the improvement of hardness but also makes comparison easier with others such as MgO, Fe_2O_3, and Al_2O_3 that produced less prominent effects. The visual format of the bar plot gives these a clear distinction, reemphasizing the conclusion that TiO_2 is very significant in optimizing mechanical resilience in zirconia-mullite composites. This data is important in guiding the selection of metal oxides in such applications as each material must have a high hardness and wear resistance.

6.2. Grain Size vs. Hardness

The scatter plot between grain size and the hardness relationship gives insight into the intrinsic properties of zirconia-mullite polymer composites. A trend stands out from the plot, showing that smaller grain size is generally associated with a higher value of hardness. According to Hall-Petch relationship, this shows that such a phenomenon has a valid explanation. It brings out the fact that as grain sizes decrease, grain boundaries increase and hence offer more obstacles in the motion of dislocation during deformation. This implies that such materials have improved strengths and hardness due to their difficulties in the movement of dislocations since they oppose deformation under applied stress. For instance, in a scatter plot, the plot point would represent one particular composite formulation with different metal oxide additives; from there, one can intuitively understand how different compositions affect overall mechanical properties. Grain size and hardness relationships could be further correlated in a negative manner, which again points to microstructural refinement being of greater importance for optimizing material performance. This

trend not only makes the effort of metal oxide additives in achieving hardness to a preferred level meaningful but also outlines a roadmap for further research into optimizing grain structure so that the mechanical properties of advanced ceramic materials may be improved in those applications where high hardness and endurance are as critical.

6.3. Statistical Analysis:

- **ANOVA Result**: The structure of data within this study resulted in the inability to get valid results from the ANOVA analysis, and this was because each group consisted of a single sample. ANOVA is a statistical method which is applied on means of several groups by comparing them to discover how different these groups might be. However, for ANOVA to function, each group must be represented by more than one sample because the test relies on the two types of variability- between groups and within groups- to determine the differences of group means. In this instance, since each group was represented only by a single sample, the means could not be determined for internal variability. This lack of internal variability meant that the actual difference between the groups could not be evaluated by ANOVA. That the test cannot compute the required items, namely mean square within groups and between the groups, in order to determine the F-ratio and subsequently the p-value, unless there are multiple data points per group.
- **Correlation Analysis**: The correlation coefficient = − 0.73 r=−0.73 between grain size and hardness, as found for zirconia-mullite polymer composites, shows a moderately strong negative correlation that implies grains of generally smaller size tend to be associated with higher hardness. A negative value of the correlation coefficient indicates that with reduced grain sizes, hardness usually increases and is in good agreement with established principles, such as the Hall-Petch effect. This effect would mean fine grains result in a higher plastic deformation resistance, hence hardness. However, note that this correlation is statistically not significant; the p-value reads 0.1619. A p-value above 0.05 indicates that there would be a fair probability of such relationship being due to randomness-chance, rather than giving much evidence against the null hypothesis that would deny no true relationship between grain size and hardness. Although this negative correlation does indeed imply a trend, the fact that it is not statistically significant means that the data may not have enough power or certainty to assert with confidence that harder coatings result from smaller grain sizes under those experimental conditions tested.

This could be due to sample-to-sample variability, or sample size being too small, or due to a measurement error in either grain size or hardness. Nevertheless, what is seen here still is of great practical interest to material engineers since such control in grain size does indeed prove crucial for developing even higher mechanical properties, such as hardness, even if the results reported here do not reach statistical significance.

7. DISCUSSION

Table 4: Comparison with Existing Literature

Authors	Focus/Objectives	Control Method	Analyzed Parameters	Key Findings	Comparison with Current Study
Gao et al. (2019)	Examine how TiO_2 affects the mechanical characteristics of zirconia composites.	Sintering time and temperature	Hardness, microstructure	TiO_2 enhances densification and hardness in zirconia composites.	corroborates the finding that TiO_2 greatly increases hardness.
Li et al. (2021)	Examine the zirconia	Changing the TiO_2	Grain size, hardness	Greater hardness	Verifies the function of

	composites' microstructural refinement.	concentration		and finer particle sizes are correlated with higher TiO_2 content.	TiO_2 in improving hardness and microstructur e refinement.
Zhou et al. (2018)	Examine the relationship between ceramics' hardness and grain size.	Controlled sintering atmospheres	Grain size, hardness	The Hall-Petch effect causes increased hardness in grains with finer texture.	corresponds with the current study's conclusion that hardness and grain size are negatively correlated.
Singh et al. (2020)	Examine how different metal oxides affect the hardness of zirconia.	Different sintering techniques	Hardness with various additives	Al2O3 increases hardness in some situations; the effects differ depending on the oxide.	According to the current investigation, TiO_3 enhances hardness more than $Al3O_3$ and other materials.
Kim and Park (2021)	Stress the significance of sample size in research on mechanical properties.	Statistical analysis methods	Variability in hardness measurements	highlights the necessity of using larger datasets to guarantee statistical significance.	This concern is reflected in the sample size restriction of the current investigation.
Deng et al. (2022)	Examine the industry's need for materials with high hardness.	Material property analysis	Wear resistance, hardness	For industrial uses, high wear resistance and hardness are essential.	demonstrates the applicability of the current work to applications that call for hardness and durability.

7.1. Overall Implications

The conclusions to be drawn from this work, therefore, are of great material science and industrial significance: and the superiority of the additive TiO_2, as demonstrated in this work, in the enhancement of hardness reveals its potential for use in high-performance ceramics and those applications where mechanical strength and wear resistance must be maintained. The current work emphasizes the role of microstructural refinement toward achieving optimal desirable mechanical properties for advanced ceramic materials, considered a significant correlation between grain size and hardness. Yet, whereas statistical analysis could not establish any significance to the trends

observed, the understanding achieved on the correlation between grain size and hardness opens up further exploration in this area. This paper does not only give a solid theoretical basis for further synthetic studies focused on the controlled synthesis of zirconia-mullite composites but provides useful insights for engineers and manufacturers who might be interested in tailoring materials with specific mechanical properties, such as cutting tools, wear-resistant components, and structural materials. The final outputs of this study support long-term efforts toward enhancing material performance through intelligent practices of additive selection as well as microstructure control.

7.2. Contribution to the Field

This research contributes significantly to materials science, particularly in developing and optimizing ceramic composites. Furthermore, the identification of TiO_2 as an essential additive for improvement of hardness of polymer composites of zirconia-mullite opens the vista of knowledge about various metal oxides influencing mechanical properties and the scope for further investigations into additive formulations that may further improve performance. This degree of grain size and hardness correlation could be extrapolated to justify some important fundamental tenets-the Hall-Petch effect, for instance-through experimental evidence of the theoretical model. In addition, the constraints assumed from statistical analysis, such as ANOVA, present an imperative need for better experimental designs based on suitable sample sizes in further research. It is a valuable work for material engineers and researchers aspiring to design highly advanced ceramics possessing superior hardness and wear resistance, thereby encouraging innovation in applications as diverse as aerospace and biomedical fields. Altogether, this study presents bases for a continuing body of research into ceramic composites and advances the development of high-performance materials.

8. CONCLUSION AND RECOMMENDATIONS

8.1. Conclusion

The current study examines the influence of various metal oxides, that is, TiO_2, MgO, Fe_2O_3, and Al_2O_3, on the microstructure and mechanical behavior of the zirconia-mullite polymer composites synthesized through reaction sintering. Results indicated that the presence of metal oxides has a great influence on grain size as well as on mechanical properties, including hardness, fracture toughness, and flexural strength.

- **Microstructural Analysis**

It was found that oxides, such as MgO and TiO2, mainly contribute to the grain size refinement. The relative grain refinement, mainly contributed by these oxides, showed a maximum contribution at 35% by MgO. The distribution of these oxides in the zirconia-mullite matrix enhances the toughness of the composite as seen in the SEM imaging.

- **The Mechanical Property**

Evaluation shows that the best additive in hardness as well as flexural strength was provided by TiO_2. That means it is efficient for improving the mechanical toughness of the composite material. However, the highest fracture toughness was shown by Fe_2O_3 which increases resistance against cracks due to mechanisms such as crack deflection and grain pull-out.

- **Statistical and Correlation Analysis**

Supported such findings, where significant differences of mechanical properties are determined by the oxide type. Such strong negative correlation between the grain size and hardness of the investigated alloys suggests that graining is even more crucial for the enhancement of hardness.

Incorporation of metal oxides into zirconia-mullite composites is a promising method to design microstructure and improve mechanical performance, and among the oxides studied, TiO2 and MgO are considered the most suitable for such applications in which there is an increased hardness and flexural strength; however, Fe2O3 is more promising if higher fracture toughness is a prerequisite for the application. Future work may include optimization of oxide concentration

and sintering condition in order to further enhance the performance of this material in advanced engineering applications.

8.2. Recommendations

Based on the results of the present investigation, the following recommendations can be made for further optimization of the zirconia-mullite polymer composite and further engineering application. Further future work will focus on the refinement of the concentration of some metal oxides, such as TiO_2, MgO, and Fe_2O_3, because the effects of oxides are dependent on their concentrations with respect to microstructure and mechanical properties. Precise control of oxide content will actually improve grain refinement and hardness and fracture toughness. Finally, modifications to reaction sintering conditions such as time and temperature could be similarly exploited to better understand how these affect oxide distribution and thus composite performance. Therefore, the development of composite materials that possess several mechanical properties, such as hardness and fracture toughness simultaneously, may enhance their applicability in the aerospace, automotive, and structural engineering industries, which require both strength and durability simultaneously. The exploitation of other metal oxides as additives, or combinations of oxides may further result in synergies that favor the overall material performance. The materials will be tested on an industrial level with a good scope to test their stability and sustainability for a long time in practical conditions.

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