

Production and Characterization of AA6061/CNT/ZrO₂ Composite Materials

Yakup KUTUPOĞLU^{1*}, Hakan ADA^{2*}, Alihan ÇETİNKAYA^{2*}, Nihat KAYA^{3*}

¹Gazi University, Graduate School of Natural and Applied Sciences, Dept. of Met. and Materials Eng., Ankara, Türkiye.

²Gazi University, Faculty of Technology, Department of Met. and Materials Eng., Ankara, Türkiye.

³Osmaniye Korkut Ata University, Kadirli Vocational School, Dept. of Machine Program, Osmaniye, Türkiye.

In this study, considering the limited number of studies in the literature, composite materials with AA6061 matrix and CNT - ZrO₂ reinforcement were produced by the PM method, and microstructural and mechanical characterizations of the produced materials were carried out. At the microstructural characterization stage, the samples were subjected to Optical Microscope (OM) examinations and at the mechanical characterization stage, hardness tests were applied to the samples. Dry wear tests were also performed on the samples to determine their wear behaviour.

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*Corresponding author: hakanada@gazi.edu.tr

1. Introduction

Today, the need for advanced technology materials is increasing rapidly. Metal matrix composite (MMC) materials have an important place due to their superior mechanical properties. The need for engineering materials that can operate above the use temperatures of conventional engineering materials and have higher specific strength has led to the development of MMC materials [1]. MMC materials are formed by the macro-level combination of the matrix and the reinforcing materials around the matrix [2]. The structure and properties of these materials are shaped depending on the matrix material, reinforcement material and interfacial bonding [3,4]. MMCs can be obtained by different production methods. One of these methods is powder metallurgy. Powder metallurgy enables metal or ceramic powders to be combined into products by mechanical and thermal effects. Low processing temperatures, near-net shape and homogeneous reinforcement distribution in the matrix are the major advantages of this method [5-7]. Metals such as Al, Mg, Cu, Ti and their alloys are generally used as matrices in MMC materials. Aluminum (Al) and its alloys are

important among engineering materials with their light weight, high thermal and electrical conductivity, corrosion resistance and strength enhancement capabilities [8].

Al alloys, which were initially used in the automotive, marine and aerospace sectors, have started to be used in the defence industry due to their increased strength and impact resistance.

To improve the strength and impact properties of Al and its alloys, composites with Al matrix are produced by adding ceramic particles (e.g. SiC, Al₂O₃, B₄C, etc.) [2,8]. AA6061 alloy combines strength and toughness with good corrosion resistance [1]. AA6061, containing Mg and Si, is a suitable matrix alloy for MMCs. Carbon nanotubes (CNTs) are tubular carbon structures with diameters on the nanometer scale. CNTs are classified as single-walled nanotubes (SWNT), multi-walled nanotubes (MWNT) and double-walled nanotubes (DWNT) [9,10]. Theoretical and experimental studies reveal that CNTs are the most unique and versatile materials ever discovered [11]. Besides their outstanding mechanical properties, CNTs have a high aspect ratio, excellent chemical stability, and superior thermal and electrical properties [12]. Many researchers have been trying

to develop advanced CNT-based composites using metals, polymers and ceramic matrix phases; Al and Mg, in particular, have attracted great interest as metal matrices [13]. Magnesium is the lightest structural metal and has the potential to produce excellent metal matrix composites with lightweight reinforcing materials such as CNTs with exceptional mechanical properties [14]. Zirconium oxide (ZrO_2) is of great interest in many fields such as fuel cell technology [15], catalyst or catalyst supports [16], protective coatings for optical mirrors and filters [17], biomaterial [18] and thermal barrier coatings [19]. The crystal structure of ZrO_2 significantly affects its physical properties. ZrO_2 has a cubic crystal structure at high temperatures above 2370 °C, a tetragonal crystal structure between 1150 °C and 2370 °C, and a monoclinic crystal structure at temperatures below 1150 °C. The monoclinic form, in particular, is found to be a thermodynamically stable phase [20]. Literature studies on ZrO_2 and/or CNT-reinforced composite materials with AA6061 matrix produced by powder metallurgy method show that various reinforcements have been used to improve the mechanical and tribological properties of these materials. Moustafa et al [21] investigated the tribological behavior, density, hardness and compressive strength of Al-4.2-Cu-1.6Mg matrix nanocomposites reinforced with ZrO_2 particles by powder metallurgy method. In the study by Farooqi et al [22], hybrid aluminum matrix composites containing carbon nanotubes (CNTs) and zirconium diboride (ZrB_2) particles were fabricated by solid-state powder metallurgy method and mechanical and tribological properties were evaluated. These studies demonstrate the breadth and depth of research on the fabrication and properties of ZrO_2 and/or CNT-reinforced composites with AA6061 matrix.

In this study, considering the limited number of studies in the literature, composite materials with AA6061 matrix and CNT - ZrO_2 reinforcement were produced by the PM method, and microstructural and mechanical characterizations of the produced materials were carried out. At the microstructural characterization stage, the samples were subjected to Optical Microscope (OM) examinations and at the mechanical characterization stage, hardness tests were applied to the samples. Dry wear tests were also performed on the samples to determine their wear behaviour.

2. Experimental Studies

2.1. Materials

In this study, AA6061 alloy (0-100 mesh) was selected as the matrix material due to its excellent processability, high specific strength, heat resistance, favourable strength-to-weight ratio, and superior wear and damage resistance. CNT (28-48 nm) and ZrO_2 (20-30 nm) were chosen as reinforcement materials for their remarkable properties, including high performance, lightweight nature, durability, and versatility. Initially, the powder mixtures were prepared according to the ratios specified in Table 1, weighed using a precision balance, and made ready for mixing.

Table 1: Mixing ratios of the powders used in the study

Sample no	Material name	AA6061 (%)	ZrO_2 (%)	CNT (%)
1	Unreinforced AA6061	100	-	-
2	%94 AA6061 %6 ZrO_2	94	6	-
3	%99,5 AA6061 %0.5 CNT	99,5	-	0,5
4	% 93,5 AA6061 %6 ZrO_2 %0.5 CNT	93,5	6	0,5

2.2. Method

AA6061 alloy without reinforcement, as well as AA6061/ ZrO_2 , AA6061/CNT, and AA6061/ ZrO_2 /CNT composite materials produced via the powder metallurgy (PM) method were analyzed for density, microstructure, hardness, and wear properties. Density measurements were carried out using Archimedes' principle, while microstructural analysis was performed with a Leica DM 4000M Optical Microscope (OM). Hardness tests were conducted using an Emcotest Duravision 2000 device following the ASTM E10 standard. The wear behaviour of the materials was evaluated through abrasive wear tests using the pin-on-disk method on a Tribometer device, adhering to the ASTM G99 standard. Brinell hardness measurements were taken using a 2.5 mm diameter penetrator tip under a 31.25 kg load, with five readings averaged for accuracy. The abrasive disk employed in the wear tests was made of AISI 52100 steel, had a hardness of 60 HRC, and was used under test conditions of 10 N load, an 800-meter sliding distance, and a speed of 1.2 m/s. Weight loss measurements were used to assess wear behaviour after the tests. The equipment utilized in the experimental studies is shown in Figure 1.



Figure 1: The devices used for the experimental studies

3. Results and Discussion

The results and findings obtained within the scope of density measurement, OM images, hardness and wear tests obtained from CNT and ZrO_2 reinforced composite materials together with unreinforced AA6061 alloy produced within the scope of this study are given in the following titles, respectively.

3.1. Density Measurements

Before microstructure, hardness and wear tests, the theoretical densities of unreinforced AA6061 alloy and AA6061/CNT, AA6061/ ZrO_2 and AA6061/CNT+ ZrO_2 composite materials were calculated by the rule of mixtures

and the experimental densities were calculated by measuring dry and wet weights by liquid flooding method according to Archimedes' principle. The data obtained from density measurements are given in Table 2, theoretical and experimental densities in Figure 2, and relative densities and porosity in Figure 3, respectively.

Table 2: Densities of materials

Sample no	Materials	Theor. density (gr/cm ³)	Exper. density (gr/cm ³)	Relat. density (%)	Poros (%)
S1	%100 AA6061	2,70	2,65	98,08	1,92
S2	%94 AA6061 %6 ZrO ₂	2,88	2,68	93,09	6,91
S3	%99,5 AA6061 %0,5 CNT	2,70	2,60	96,27	3,73
S4	%93,5 AA6061 %6 ZrO ₂ %0,5 CNT	2,88	2,70	93,95	6,05

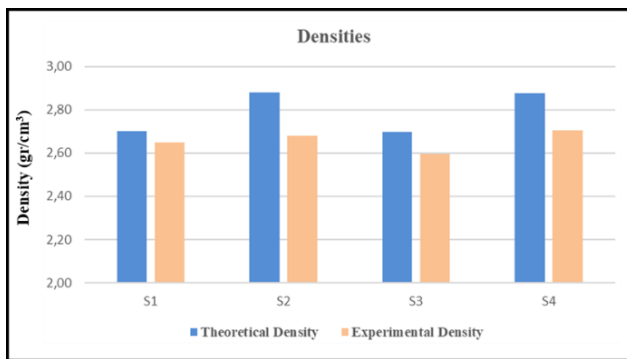


Figure 2: Theoretical and experimental densities of the samples

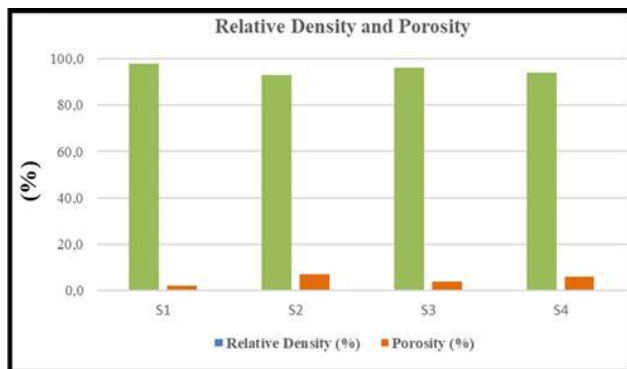


Figure 3: Relative density and porosity of the samples

In the density measurements given in Table 2 and the graphs in Figure 2 and Figure 3; 100% AA6061 alloy has a high density and low porosity, which shows that a homogeneous structure is provided. While the theoretical density increased or did not change with adding ZrO₂ and CNT in S2 and S3 samples, the experimental density remained at lower values. This indicates that there may be problems in the distribution of reinforcement particles in the composite; more voids (porosity) are formed, and compression is not

fully achieved. In specimen S4, the porosity remained relatively high (6.05%) with the combined use of ZrO₂ and CNT. This may indicate that hybrid ZrO₂ and CNT reinforcement may create more voids in the sintering or compression processes. 100% AA6061 (S1) had the lowest porosity (1.92%) and gave the most efficient results in terms of density. The addition of ZrO₂ (S2 and S4) and CNT (S3 and S4) increased the theoretical density but increased the amount of porosity and decreased the experimental density. This indicates that the fabrication method needs to be optimized for such reinforcements. Relative density values were in the range of 93-98% for all samples. This shows that the composites have a good density ratio overall.

3.2. Microstructure Investigations

Optical microscope images of the produced composite samples are given in Figure 4. OM images were taken at 200 and 500 magnifications and interpreted comparatively. In the OM images, S1 represents 100% AA6061 alloy, S2 represents 94% AA6061 - 6% ZrO₂, S3 represents 99.5% AA6061 - 0.5% CNT and S4 represents 93.5% AA6061 - 6% ZrO₂ - 0.5% CNT composite materials.

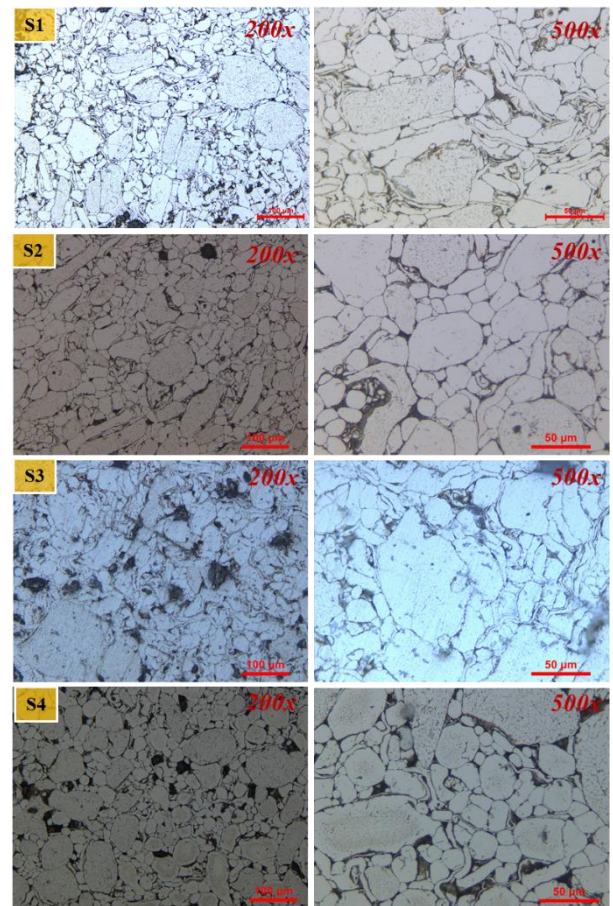


Figure 4: OM images of composite materials (S1: %100 AA6061, S2: %94 AA6061, %6 ZrO₂, S3: %99,5 AA6061, %0,5 CNT, S4: %93,5 AA6061, %6 ZrO₂, %0,5 CNT).

The optical microscopy (OM) images of composite materials with an AA6061 matrix and CNT-ZrO₂

reinforcement are presented in Figure 4. Sample S1 displays a uniformly distributed matrix structure made entirely of AA6061 alloy in these images. The minimal presence of pores or secondary phases indicates that the sintering process and the interface formation have proceeded as expected. Additionally, the grains in the unreinforced AA6061 alloy are clearly distinguishable, and the phase boundaries are well-defined. In the OM images of the 6% ZrO₂ reinforced S2 sample, ZrO₂ particles are visible as dispersed dark regions within the AA6061 matrix. Given that the reinforcement particles are nano-sized, the observed structures likely consist of agglomerated ZrO₂ particles. These particles are not evenly distributed but are instead clustered in certain areas, which may suggest issues such as incomplete dispersion or particle agglomeration. Sample S3 represents a composite material made up of 99.5% AA6061 alloy and 0.5% CNT reinforcement. As documented in the literature, CNT typically forms fine, network-like structures. The dark areas observed in the OM image may indicate CNT clustering or accumulation in the intergranular regions. Although CNT is used in small amounts, it is a reinforcing material that can be difficult to distribute uniformly. Therefore, ensuring a homogeneous distribution of CNT in the matrix is crucial for optimizing the properties of composite materials.

3.3. Hardness Test Investigations

Hardness tests were performed on composite samples to determine the resistance of ZrO₂ and CNT-reinforced Al matrix composite materials to plastic deformation. The average values of the hardness values obtained as a result of the tests are given in Figure 5.

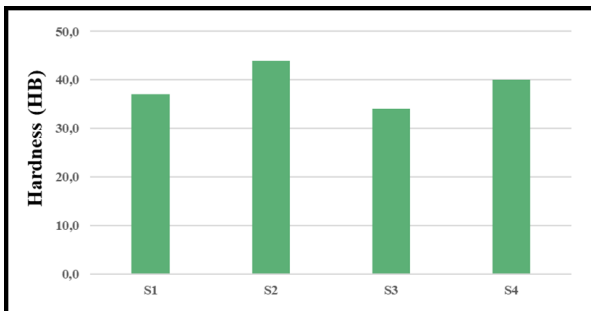


Figure 5: Hardness test values of materials

From the hardness graph given in Figure 5, it can be concluded that the hardness-increasing effect of ZrO₂ is quite strong, while CNT makes a limited contribution to this increase. When the hardness result graph is analyzed in detail, it is seen that the hardness value of sample S1 is about 35 HB, which shows that pure AA6061 alloy is the main reference in terms of hardness. The unreinforced material presented a relatively lower hardness value than the reinforced ones. The hardness value of specimen S2 exceeded 40 HB. This indicated that the hardness increased significantly with the addition of ZrO₂. The ceramic properties and high hardness of ZrO₂ may have led to this improvement in the matrix. The hardness value of sample S3

was slightly higher than that of S1 and was observed to be about 37 HB. The addition of CNT caused a slight increase in hardness but was not as effective as ZrO₂ doping. This indicated that CNT contributed mechanically to the structure, but its potential to increase hardness was lower than ZrO₂. In specimen S4, the hardness value is around 40 HB, almost at the same level as S2. The combination of both ZrO₂ and CNT increased the hardness, but this increase did not provide any extra improvement compared to S2. This implies that the effect of ZrO₂ on hardness is dominant, and the contribution of CNT is limited.

4. Wear Test Investigations

ZrO₂ and CNT-reinforced Al matrix composite materials were subjected to wear tests to examine their behaviour against wear. The graph showing the wear test results of the composite materials is given in Figure 6. The graph shows the weight loss in grams after wear for different specimens. A lower weight loss indicates that the material is more resistant to abrasion. When the data obtained from the graph is analyzed; the highest wear resistance is in the S2 sample, which shows that ZrO₂ provides effective protection against wear. The weight loss observed in sample S1 showed that the wear resistance of pure AA6061 alloy was low. Since there are no reinforcements, it is thought that the material's surface wears more due to the frictional effect. On the other hand, it was found that the wear resistance decreased in the S3 specimen due to a low reinforcement ratio and possible dispersion problems. In specimen S4; it was observed that the combination of ZrO₂ and CNT caused an increase in material strength. In this case, it can be said that ZrO₂ is the determining reinforcement element.

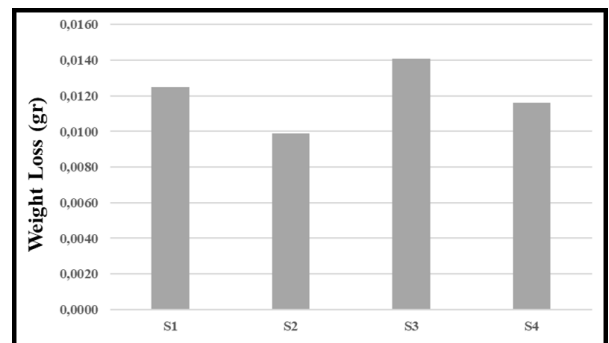


Figure 6: Weight loss obtained from wear tests of composite materials

5. Conclusions

In this study, hybrid composite materials with AA6061 matrix and CNT - ZrO₂ reinforcement were fabricated using PM technique. The materials' density, microstructural properties, hardness and wear behaviours were investigated in detail. The results obtained from the study are reported as follows.

➤ The S1 sample exhibited the highest density and lowest porosity, indicating a well-homogenized structure. However,

the theoretical density either increased or remained constant for the samples with added reinforcements (ZrO₂ and CNT), while the experimental density was lower. This resulted in increased porosity, especially in S4, which combined both ZrO₂ and CNT.

➤ In the OM images, S1 displayed a uniform matrix with minimal porosity, confirming effective sintering. For the ZrO₂-reinforced S2, the presence of agglomerated ZrO₂ particles indicated incomplete dispersion. In S3, CNT appeared to form clusters.

➤ The hardness results revealed a significant increase in hardness for the S2 sample, where ZrO₂ was added, reaching a value above 40 HB. The addition of CNT (S3) resulted in a slight hardness increase but was less effective than ZrO₂. Combining both reinforcements in S4 led to an increase in hardness, but the effect of ZrO₂ was dominant, with CNT contributing minimally.

➤ The wear resistance data showed that ZrO₂ (S2) significantly improved wear resistance, while the unreinforced AA6061 alloy (S1) exhibited poor wear performance. The S3 sample, with a low CNT ratio and potential dispersion issues, showed reduced wear resistance. In S4, the combination of ZrO₂ and CNT enhanced wear resistance, but ZrO₂ remained the primary reinforcement responsible for this improvement.

The experimental results suggest that the addition of ZrO₂ significantly improves both the hardness and wear resistance of the AA6061 alloy, with ZrO₂ acting as the dominant reinforcement. CNT, while contributing to mechanical strengthening, had a limited effect on hardness and wear resistance compared to ZrO₂. The composites overall exhibited good density and wear resistance, with relative density values between 93-98%, highlighting their potential for industrial applications.

References

- [1] Özçatalbaş Y, Köse D (2021) The effect of super solidus liquid-phase sintering processes on properties of AA6061-B4C MMCp materials. *Afyon Kocatepe University Journal of Science and Engineering* 21(3):696-709. <https://doi:10.35414/akufemubid.876449>
- [2] Karakoç H, Ovalı İ, Dündar S, Çıtak R (2019) Wear and mechanical properties of Al6061/SiC/B4C hybrid composites produced with powder metallurgy. *Journal of Materials Research and Technology* 8(6):5348-5361, <https://doi.org/10.1016/j.jmrt.2019.09.002>
- [3] Karabulut H, Çıtak R, Çinici H (2013) Effect of mechanical alloying duration on transverse rupture strength of Al+10% Al₂O₃ composites. *Journal of The Faculty of Engineering and Architecture of Gazi University* 28(3):635-643.
- [4] Kalemtaş A (2014) An overview of metal matrix composites. *Putech&Composites* 22:18-30.
- [5] Asgharzadeh H, Simchi A (2009) Supersolidus liquid phase sintering of Al6061/SiC metal matrix composites. *Powder Metallurgy* 52(1):28-35.
- [6] Güven ŞY (2011) Powder metallurgy and metallic foams. *SDU Journal of Technical Science* 1(2):22-28.
- [7] Ayvaz M, Çetinel H (2014) Production and characterization of aluminum based composites by powder metallurgy method for different matrix composition and amount of the reinforcement. *CBU Journal of Science* 10(1):45-53.
- [8] Karakoç H, Çıtak R (2017) Study on weldability of B4C reinforced aluminium composite materials with TIG welding. *El-Cezeri Journal of Science and Engineering* 4(3):584–592, <https://doi:10.31202/ecjse.341098>
- [9] Topcu İ (2018) Investigation of microstructure and mechanical properties of metal matrix (MMC) composites developed with CNT reinforced aluminum matrix materials. *APJES* 6(3):164–167. <https://doi:10.21541/apjes.360028>
- [10] Iijima S (1991) Helical microtubules of graphitic carbon. *Nature* 354:56–58. <https://doi.org/10.1038/354056a0>
- [11] Pérez-Bustamante R, Estrada-Guel I, AmézagaMadrid P, Miki-Yoshida M, Herrera-Ramírez JM, Martínez-Sánchez R (2010) Microstructural characterization of Al- MWCNT composites produced by mechanical milling and hot extrusion. *J Alloy Compd* 495(2):399-402. <https://doi.org/10.1016/j.jallcom.2009.10.099>
- [12] Agnew SR, Horton JA, Lillo TM, Brown DW (2004) Enhanced ductility in strongly textured magnesium produced by equal channel angular processing. *Scripta Materialia* 50(3):377-381. <https://doi.org/10.1016/j.scriptamat.2003.10.006>
- [13] Kim WJ, An CW, Kim YS, Hong SI (2002) Mechanical properties and microstructures of an AZ61 Mg Alloy produced by equal channel angular pressing. *Scripta Materialia* 47(1):39-44. [https://doi.org/10.1016/S1359-6462\(02\)00094-5](https://doi.org/10.1016/S1359-6462(02)00094-5)
- [14] Kim WJ, Hong SI, Kim YS, Min SH, Jeong HT, Lee JD (2003) Texture development and its effect on mechanical properties of an AZ61 Mg alloy fabricated by equal channel angular pressing. *Acta Materialia* 51(11):3293-3307. [https://doi.org/10.1016/S1359-6454\(03\)00161-7](https://doi.org/10.1016/S1359-6454(03)00161-7)
- [15] Park S, Vohs JM, Gorte RJ (2000) Direct oxidation of hydrocarbons in a solid-oxide fuel cell. *Nature* 404(6775):265-267. <https://doi.org/10.1038/35005040>
- [16] Li Y, He D, Cheng Z, Su C, Li J, Zhu Q (2001) Effect of calcium salts on isosynthesis over ZrO₂ catalysts. *Journal of Molecular Catalysis A: Chemical* 175(1-2):267-275. [https://doi.org/10.1016/S1381-1169\(01\)00233-3](https://doi.org/10.1016/S1381-1169(01)00233-3)
- [17] Zhang Q, Shen J, Wang J, Wu G, Chen L (2000) Sol-gel derived ZrO₂-SiO₂ highly reflective coatings. *International Journal of Inorganic Materials* 2(4):319-323. [https://doi.org/10.1016/S1466-6049\(00\)00037-4](https://doi.org/10.1016/S1466-6049(00)00037-4)
- [18] Piconi C, Maccauro G (1999) Zirconia as a ceramic

biomaterial. *Biomaterials* 20(1):1-25.

[https://doi.org/10.1016/S0142-9612\(98\)00010-6](https://doi.org/10.1016/S0142-9612(98)00010-6)

- [19] Rahaman MN, Gross JR, Dutton RE, Wang H (2006) Phase stability, sintering, and thermal conductivity of plasma-sprayed ZrO₂-Gd₂O₃ compositions for potential thermal barrier coating applications. *Acta Materialia* 54(6):1615-1621.
<https://doi.org/10.1016/j.actamat.2005.11.033>
- [20] Gao P, Meng LJ, Dos Santos MP, Teixeira V, Andritschky M (2000) Study of ZrO₂-Y₂O₃ films prepared by rf magnetron reactive sputtering. *Thin Solid Films* 377:32-36.
[https://doi.org/10.1016/S0040-6090\(00\)01395-X](https://doi.org/10.1016/S0040-6090(00)01395-X)
- [21] Moustafa EB, Aljabri A, Abushanab WS, et al (2024) A comprehensive study of Al-Cu-Mg system reinforced with nano-ZrO₂ particles synthesized by powder metallurgy technique. *Sci Reports* 14:2862.
<https://doi.org/10.1038/s41598-024-53061-9>
- [22] Farooqi A, Ahmed M, Subhani T, et al (2019) Hybrid aluminum matrix composites containing carbon nanotubes and zirconium diboride particles: fractography, microstructure and mechanical performance. *SN Appl Sci* 1:1702.
<https://doi.org/10.1007/s42452-019-1767-7>