Anti fouling coating characterization with purified Zirconia from West Kalimantan Zircon Sand for Boiler application

Yulinda Lestari¹, Anne Zulfia², Radhian Krisnaputra³, Nareswari Novita Satiti³, Eko Sulistiyono⁴ and Efendi Mabruri⁴

¹PhD Candidate at Metallurgy and Material Engineering Department, University of Indonesia
²Metallurgy and Material Engineering Department, University of Indonesia
³Vocational school of mechanical engineering department, Gajahmada University
⁴Research Center for Metallurgy and Material, Indonesia Institute of Sciences

*E-mail: anne@metal.ui.ac.id

Abstract. Zircon sand is a mineral material for zirconia purification which can be found in Indonesia. Zirconia has various functions, one of the function applied at Boiler high temperatures. The low coefficient of zircon thermal expansion indicates high thermal shock and spalling resistance. In this study, zirconia comes from Kalimantan zircon sand was applied to an anti-fouling coating. The purified zirconia is compared with zircon sand and synthetic zirconia. The purified zirconia yields a 82.48% Zr content, compared to the zircon sand has 70.85% Zr content and 89.43% in synthetic zirconia. The substrate used for coating is ferritic steel. The coating method uses a brush coating then sintered at a temperature of 400°C and 800°C. Coatings that contained purified zirconia have a rougher surface compared to coatings that contained zircon sand and synthetic zirconia. It is because the zirconia powder granules produced have a larger size. The microstructure also shows the surface of the coating with zirconia from the purification has a tenuous structure with large granules. It shows further treatment is needed in the purification of zirconia so that the grain size is homogeneous when applied to the coating.

1. Introduction

The choice of anti fouling coating material is related to thermal conductivity which is inversely proportional to fouling resistance. If the fouling resistance is high then the thermal conductivity of the material is not too high but enough to conduct heat. Based on this, zirconia (ZrO₂) is selected as matrix and graphite lubricant is selected as filler in ceramic based composite coating material [1, 2]. Graphite has good thermal stability, the price is relatively cheap and easily combined with various matrices. In addition to the superiority of the characteristics, another reason for the use of zirconia (ZrO₂) in this study is to increase the added value of local mineral resources, zircon sand (ZrSiO₄) from West Kalimantan [3]. Zircon sand contains ZrO₂ and other metal oxides such as SiO₂, TiO₂ and Al₂O₃ which are commonly used as coating materials [4-6]. The zirconia is a mineral in Indonesia that has gone through a refining process. The low coefficient of zircon thermal expansion indicates high thermal shock resistance and resistance to spalling. Spalling is the deformation of a material due to heat shock [7]. A review of several anti-fouling coatings has been carried out by Banerjee, et al [8] but most are...
for applications in marine and the material is dominated by polymer coatings. While anti-fouling coatings on boilers and heat exchangers that operate at high temperatures are summarized by Gomes da Cruz, et al [9].

2. Experimental

2.1 Materials

The methodology stages in this study consisted of purification of West Kalimantan zircon sand, zirconia powder characterization resulting from purification and commercial zirconia powder, substrate coating with ceramic slurry and characterization of coated substrates.

2.2 Method

2.2.1. Purification of West Kalimantan Zircon Sand

ZrO$_2$ purification was carried out by zircon decomposition using an alkaline fusion method [3, 10]. The stages of the ZrO$_2$ purification process are zircon sand sifting, zircon decomposition, water leaching, acid leaching, precipitation, and calcination.

2.2.2 Characterization of Zirconia Powder

The zirconia powder characterization was done by XRF testing. This test is carried out to determine the percentage of elements (% wt) contained in ZrO$_2$ powder. Calculation of conversion of elemental percentages to percentage of oxide can be done to find out what levels of ZrO$_2$ and other oxides.

2.2.3. Substrate was coated with ceramic slurry

Ferritic steel as a substrate has the dimensions of 20x15x7 mm. Before the coating process, sand blasting is carried out on the surface of the substrate. Sand blasting aims to strengthen the bond between the steel surface and the coating [2]. Ceramic slurry is made with the composition listed in Table 1. The following composition refers to research conducted by Wang, et al. 2017. The mixing process was carried out with a magnetic stirrer for 30 minutes until evenly mixed, then ultrasonic milling was carried out on the mixture for 3 minutes as a deagglomeration process [11]. The mixture is processed further with an ultrasonic bath for 1 hour [12]. The ultrasonic bath process is followed by a mixture filtration process to minimize water content. Filtration is done to get a thicker mixture called slurry. Brush painting is the simplest method and is very possible to do when working conditions are needed where not much coating material is wasted [13]. Sintering of coated steel is carried out at 400$^\circ$C and 800$^\circ$C. The temperature selection follows the optimum temperature in a preliminary study conducted by Xiao et al. 2018 [14].

![Table 1. Composition of Ceramic Slurry Coating [2]](https://example.com/table1.png)

| Materials           | %w      |
|---------------------|---------|
| Zirconia Powder     | 12      |
| Graphite            | 2       |
| Potash Waterglass   | 18      |
| SLS Powder          | 5       |
| Aquades             | Balanced|

2.2.4. Characterization of Coated Substrates

SEM-EDAX testing was carried out to observe surface morphology coatings on steel surfaces. From EDAX results it can be seen what elements are present at a test point. The SEM-EDAX test results were used to analyze the effect of ZrO$_2$ powder types used as a mixture of ceramic slurry on the surface morphology coating that was formed, by comparing the test samples with and without sintering.

3. Results and Discussion

3.1. ZrO$_2$ Content

The XRF testing was carried out in 3 powder samples such as Kalimantan zircon sand, purified zirconia and commercial zirconia.
Table 2. XRF Test Result

| Oxide   | Kalimantan Zircon Sand | Purified Zirconia | Commercial Zirconia |
|---------|------------------------|-------------------|---------------------|
| ZrO₂    | 59.212                 | 67.986            | 76.887              |
| SiO₂    | 29.755                 | 7.923             | 1.661               |
| HfO₂    | 1.251                  | 1.387             | 1.584               |
| TiO₂    | 1.143                  | 0.5               | 0.058               |
| Al₂O₃   | 1.403                  | 2.813             | 0.253               |
| Fe₂O₃   | 0.143                  | 0.489             | 0.024               |
| P₂O₅    | 5.906                  | 16.583            | 18.758              |
| MgO     | 0.3                    | 0.473             | 0.397               |
| Y₂O₃    | 0.377                  | 0.310             | 0.0                 |

Table 2 shows zircon oxide content and other impurities. Zirconia powder contains other metal oxides which are also often used as coating materials, such as SiO₂, TiO₂ and Al₂O₃. HfO₂ is an oxide material which has high oxidation resistance that is resistant to ablation and spallation.

3.2. Visual Image of Coated Substrates
The substrate has been coated with ceramic slurry using the brush painting method, then it dried in an oven at 70°C for 30 minutes. Figure 1 shows the visual images of coated substrates.

![Figure 1](image1.png)

(a) Purified Zirconia, (b) Commercial Zirconia

From Figure 1, it shows visual differences in surface coating. Figure 1(b) has a smoother surface than Figure 1(a). In figure 1(a), the coating surface has powder particles which are agglomerate in several areas.

3.3. Comparison of Microstructures between Purified Zirconia and Commercial Zirconia Ceramic Coating
The microstructure of the surface coating was seen by SEM using a 500x magnification secondary electron imaging. The surface topography of the coating can be seen in the following image:
Figure 2 shows difference morphology surface of coating samples using commercial zirconia and purified zirconia. The surface of the commercial zirconia sample coating looks smoother and even distribution of coating particles. There are no graphite sheets which accumulate on the surface of the coating. The presence of porosity and microcrack is seen on the coating surface in Figures 2 (a) and 2 (b). ZrO$_2$ on the coating surface of figure 2 (a) is seen with light colors in small amounts and not spread evenly. This is supported by EDAX data of the elements scattered on the following surface coatings:

| Element | Purified Zirconia Coating (% Mass) | Commercial Zirconia Coating (% Mass) |
|---------|-----------------------------------|-------------------------------------|
| C       | 62.16                             | 20.46                               |
| O       | 19.39                             | 29.28                               |
| Na      | 1.12                              | 1                                   |
| Al      | 0.88                              | -                                   |
| Si      | 12.51                             | 17.85                               |
| K       | 0.75                              | 0.75                                |
| Fe      | 2.55                              | -                                   |
| Zr      | 0.64                              | 30.66                               |

From table 3, it can be seen that the purified zirconia coating is dominated by the element carbon (C) where carbon is the main constituent of graphite used as a lubricant in the ceramic slurry mixture. The oxygen element (O) represents the presence of various oxide bonds in zirconia powder samples used as a mixture of ceramic slurry. The level of Zr detected is so small that no distribution is seen on the surface of the coating. Whereas in commercial zirconia coating, zirconium element (Zr) became the most dominant constituent element with the largest mass percentage of 30.66%, followed by oxygen (O) with a mass percentage of 29.28%, carbon element (C) with mass percentage 20.46%. This supports the surface of the microstructure, that shows the very even distribution of ZrO$_2$ on the commercial zirconia coating when compared to the purified zirconia coating.

3.4. Effect of Sintering on the Microstructure Surface Coating

Sintering aims to eliminate volatiles in the ceramic layer at high temperatures. As porosity increases, there will be an increase in the contact area of the particles and their mechanical strength increases.
Figure 3. Microstructures of Sintered Coating Surfaces. (a) Purified Zirconia sintered at 400°C, (b) Purified Zirconia sintered at 800°C, (c) Commercial Zirconia sintered at 400°C, and (d) Commercial Zirconia sintered at 800°C.

Figure 3a, 3b, 3c, 3d shows microstructures of sintered purified zirconia and sintered commercial zirconia surface coating. The microstructure show that the coating particles formed are more fused and compacted so that the sample surface becomes smoother and more even than zirconia coating without sintering. The sintering coating surface has an even distribution of coating particles, a denser surface, and invisible graphite sheets. The coating surface of commercial zirconia (Figure 3c and 3d) after sintering is denser and more even when compared to samples without sintering which can be seen from the size of the microcrack that becomes narrower. This is supported by research which states that sintering causes the combining of particles which is indicated by the expansion of the particle boundary area so that a continuous area is formed [15]. But at sintering temperature of 800°C (figure 3b and 3d), visible light-colored particles begin to fade and even disappear. This can be related to the EDAX results in table 4, that the elements of Carbon and Zircon are much reduced. The dominant element on the surface of the substrate coating is Fe, this shows that the coating is peeling off and damaged. When the coating layer is too thin and sintered at very high temperatures, cracking and volume shrinkage are possible during crystallization and phase transformation [16].
Table 4. EDAX Test Result Sintered Coating

| Element | Purified Zirconia Coating Sintered at 400°C (% Mass) | Purified Zirconia Coating Sintered at 800°C (% Mass) | Commercial Zirconia Coating Sintered at 400°C (% Mass) | Commercial Zirconia Coating Sintered at 800°C (% Mass) |
|---------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| C       | 44.71                                           | 3.07                                            | 12.27                                           | 5.34                                            |
| O       | 28.25                                           | 19.29                                           | 31.43                                           | 21.26                                           |
| Na      | 1.56                                            | 8.51                                            | 2.64                                            | 11.36                                           |
| Al      | 1.06                                            | -                                               | -                                               | -                                               |
| Si      | 20.2                                            | 1.12                                            | 16.42                                           | 0.85                                            |
| K       | 1.23                                            | -                                               | 0.98                                            | -                                               |
| Mn      | -                                               | -                                               | -                                               | 2.37                                            |
| Fe      | 2.14                                            | 68.01                                           | 2.22                                            | 57.77                                           |
| Zr      | 0.86                                            | Very low                                        | 34.04                                           | 1.04                                            |

4. Conclusion
The result of coating with purified zirconia has a morphology rougher than commercial zirconia. Commercial zirconia has a more even coating particles and coating-forming elements. Commercial zirconia has a higher and more even zircon element when applied as a coating. This is because zirconia from purification has granular particles which are still coarse. So that purified Zirconia is produced from the alkaline fusion method still requires further treatment if it is to be applied as a coating. Whereas Sintering temperature of 400°C produces a finer micro-coating structure and closes the micro-crack formed on the coating that is not sintered. But Sintering temperature of 800°C damages the coating on the substrate so that a lot of peeling is indicated by the forming elements of the coating being slightly on the substrate.

Acknowledgement
The Authors would like to thank to PDD Funding of Kemenristekdikti who have funded this research.

References
[1] Bahaaideen F B, Ripin Z M and Ahmad Z A 2010 Electroless Ni-P-C₆(graphite)-SiC Composite Coating and its Application onto Piston Rings of a Small Two Stroke Utility Engine (Journal of Scientific & Industrial Research) 69, p 830-834
[2] Wang J, Yuan Y, Chi Z, and Zhang G 2017 Development and application of anti-fouling ceramic coating for high-sodium coal-fired boilers (Journal of the Energy Institute)
[3] Artisantri L 2018 ZrO₂ Formation through NaOH Alkali Decomposition and HNO₃ Leaching (Thesis, Sultan Ageng Tirtayasa University)
[4] Nguyen M D, Bang J W, Kim Y H, Bin A S, Hwang K H, Pham V H, and Kwon W T 2018 Slurry Spray Coating of Carbon Steel for Use in Oxidizing and Humid Environments (Ceramics International) 44 (7), p 8306-8313
[5] Oldani V, Del Negro R., Bianchi C L, Suriano R, Turri S, Pirola C, and Sacchi B 2015 Surface properties and anti-fouling assessment of coatings obtained from perfluoropolyethers and ceramic oxides nanopowders deposited on stainless steel (Journal of Fluorine Chemistry) 180, p 7-14
[6] Srinivasulu K and Sa MV 2016 Advanced Ceramic Coatings on Stainless Steel: A review of Research, Methods, Materials, Applications and Opportunities (International Journal of Advanced Engineering Technology) 7, p 141
[7] Ayala L 2015 Technical handbook on zirconium and zirconium compounds (Zircon Industry Association)
[8] Banerjee L, Pangule R C, and Kane R S 2011 Antifouling coatings: recent developments in the design of surfaces that prevent fouling by proteins, bacteria, and marine organisms (Advanced Materials) 23, p 690-718

[9] da Cruz L G, Ishiyama E, Boxler C, Augustin W, Scholl S, and Wilson D 2015 Value pricing of surface coatings for mitigating heat exchanger fouling (Food and Bioproducts Processing) 93, p 343-363

[10] Liu J, Song J, Qi T, Zhang C and Qu J 2016 Controlling the formation of Na$_2$ZrSiO$_5$ in alkali fusion process for zirconium oxychloride production (Advanced Powder Technology) 27(1), p 1-8

[11] Bittmann B, Haupert F, and Schlarb A K 2009 Ultrasonic dispersion of inorganic nanoparticles in epoxy resin (Ultrasoundics Sonochemistry) 16, p 622-628

[12] Billotte C, Fotsing E R, and Ruiz E 2017 Optimization of Alumina Slurry for Oxide-Oxide Ceramic Composites Manufactured by Injection Molding (Advances in Material Science and Engineering, Hindawi Publishing Corporation)

[13] Ulaeto S B, Rajan R, Pancrecious J K, Rajan T P D and Pai B C 2017 Developments in smart anticorrosive coatings with multifunctional characteristics (Progress in Organic Coatings) 111, p 294-314

[14] Xiao K, Xue W, Li Z, Wang J, Xueming Li, Dong C, Wu J, Xiaogang Li, and Wei D 2018 Effect of Sintering Temperature on the Microstructure and Performance of a Ceramic Coating Obtained by the Slurry Method (Ceramics International) 44(10), p 11180-11186

[15] Nguyen P, Harding S, and Ho S Y 2007 Experimental studies on slurry based thermal barrier coatings (Eng. Aust) 1, p 545-550

[16] Dai Y, Yin Y, Xu X, Jin S, Li Y, and Harmuth H 2018 Effect of the phase transformation on fracture behaviour of fused silica refractories (Journal of the European Ceramic Society) 38(16), p 5601-5609