Microstructural and mechanical characteristic of ceramic composite coating developed by electrophoretic deposition

R D Desiati\textsuperscript{1,2,}\textsuperscript{*}, A Anawati\textsuperscript{1} and E Sugarti\textsuperscript{2}

\textsuperscript{1} Department of Physic, Faculty of Mathematics and Natural Science, University of Indonesia, Depok, 16424, Indonesia
\textsuperscript{2} High Resistant Material Research Group, Research Center for Physics, Indonesian Institute of Sciences (LIPI), Serpong, 15314, Indonesia

\*resetiana.dwi.desiati@gmail.com

Abstract. Ceramic-composite coating consisted of Yttria Stabilized Zirconia (YSZ), Fe\textsubscript{2}O\textsubscript{3} and aluminum powder has been successfully formed on Inconel 625 substrate by electrophoretic deposition (EPD). The coating density depends not only on the stability of the EPD suspension but also on the applied voltage. In the present study, a single stage voltage treatment at 60V and a two-stage voltage treatment at 30V followed by 60V of the EPD were used. A fresh green body of ceramic coating was dried at room temperature for 24 hours prior to heat-treated at temperature of 1200 \textdegree C for 4 hours with heating rate of 2\textdegree C/min using horizontal heated furnace under argon gas inert. The effect of single- and two-stage treatments on the microstructural and mechanical hardness of the coating were investigated by Field Emission-Scanning Electron Microscopy and Vickers hardness test, respectively. The elemental composition of the coating was analysed by Energy Dispersive Spectroscopy and the crystalline phases were identified by x-ray diffractometer. The results showed that a less porous structure, and therefore, higher hardness was observed on the coating formed by a two-stage voltage than that of resulting from a single-stage voltage. The crystalline phase formed on the coatings was dominated by a tetragonal phase of ZrO\textsubscript{2}.

1. Introduction
Ceramic coatings are widely used to improve the structural integrity of metals such as wear resistance, corrosion resistance, and high thermal stability [1]. Generally, ceramic coatings are deposited as a topcoat layer in the thermal barrier coating (TBC) system on a nickel-base superalloy substrate [2]. One type of ceramic material that is commonly used are fine ceramics of zirconia which is stabilized by yttria, namely Yttria Stabilized Zirconia (YSZ) because it has the ability to improve mechanical properties. They are several methods that can be used for developing Thermal Barrier Coating systems such as Air Plasma Spray (APS), Electron Beam Physical Vapor Deposition (EBPVD), Combustion Chemical Vapor Deposition (CCVD), etc. Those methods require high production costs and complex equipment. Therefore, Electrophoretic Deposition (EPD) is considered a suitable method for the ceramic coating deposition due to low-cost procedure, highly versatile, and uniformly deposit ceramic coating [2,3]. The thickness produced by EPD is approximately of 1 – 50 \mu m [4]. Applied voltage is a key variable besides other parameters affecting the coating thickness. It has been well known that good quality of coating deposition is produced by applying voltage under 100 volts in the EPD process [5]. In addition, applied high voltage causes a high electric field which makes the particle suspension of
ceramic materials quickly deposit to the substrate, thus it will be a factor to bad quality of the deposition such as high porosity, unexpected structure, cracks, etc. [5]. As reported by Meng et al, the application of dynamic voltage can be formed a solid and uniform on the inner layer by smaller particles while larger particles form a porous layer on the outside layer. The difference in density is achieved due to the influence of electrophoresis velocity, electric field, and particle size [6]. Higher electric fields produce porous and coarse layers while lower electric fields produce denser layers with finer particle sizes [6].

The addition of Fe$_3$O$_4$ as a sintering aid can decrease the temperature of YSZ due to promote the formation of dense tetravalent oxides as reported by Bai et al [7]. The mechanical properties of sintered YSZ significantly improved with Fe$_3$O$_4$ addition. Moreover, the addition of Fe$_3$O$_4$ will also contribute to strengthening the ceramic layer and reduce further propagation of the cracks in the coating system.

Therefore, the purpose of the present paper is to investigate the microstructure and mechanical properties of a YSZ with Fe$_3$O$_4$ addition deposited by the EPD method with the dissimilar treatment of applied voltage, specifically two-stage and single-stage of voltage treatment under 100 volts.

### 2. Experimental methods

The ceramic suspension was prepared by mixing of 93.6 wt% commercially 3YSZ powder (3 mol% Y$_2$O$_3$, > 99%, Kanto, Japan), 0.8 wt% Iron (III) oxide (2 mol% Fe$_3$O$_4$, > 99%, technical powder), 0.9 wt% Al powders (> 99%, Kanto, Japan) and 4.7wt% iodine as a dispersant. Acetyl acetone (ACAC, >99%, Merck) and ethanol (Et >99%, Merck) with a volume ratio of 1:1 was utilized as solvents to prepare the ceramic suspension. Prior to the EPD process, the suspension was magnetically stirred for 120 h followed by homogenizer for 1 h and sonication for 5 min.

EPD process was performed in the cathodic process which Inconel 625 (IN625) as a cathode and nickel plate as an anode. Two different of voltage treatment were carried out during the EPD process with a parameter of two-stage at 30 volts followed by 60 volts for 3 min in each stage and a single stage at 60 volts for 6 min as shown in figure 1. The green coatings were dried at room temperature for 24 h subsequently sintered at a temperature of 1200 °C for 4 h with heating rate of 2 °C/min in argon gas inert condition.

Characterization was carried out using FE-SEM (JEOL, JIB4610F) for surface and cross-sectional microstructures and EDS (Oxford, X-MAX 50) for elemental distribution of the coating samples. Phase formed on the coating was identified by XRD (Smartlab, Rigaku) with a Cu Kα radiation (wavelength, 1.5405 Å) operated at 40 kV and 30 mA for 20 starts from 10° to 90°. The hardness of the coating was measured using micro vickers hardness (LECO Corp, FMX 2635) by applying a 500 gf for 13 seconds.

![Figure 1](image_url) 

**Figure 1.** Dissimilar treatment of applied voltage during the EPD process: (a) two-stage and (b) single stage.

### 3. Results and discussion

#### 3.1. Microstructure and element distribution

Figure 2 shows the surface morphology of Fe$_3$O$_4$ doped Yttria Stabilized Zirconia (3YSZ) coating on Inconel 625 after sintering at a temperature of 1200 °C for 4 h. The surface morphology on the two-
stage coating sample revealed that the particles were denser and larger than on the single stage of the coating sample. This may occur when the EPD process initiated at low voltage, small particles preferred to adhere to the surface of the substrate followed by depositing large particles at high voltage [8]. As a results, small particle seems imparted the porosity, thus the surface became denser.

**Figure 2.** Surface morphology of Fe$_2$O$_3$ doped 3YSZ coating after sintering at a temperature of 1200 °C for 4 h: (a) two-stage and (b) single stage of voltage treatment.

In addition, Figure 3 shows a cross-sectional microstructure and element analysis of Fe$_2$O$_3$ doped 3YSZ coating. A Thermally Grown Oxide (TGO) layer formed between the ZrO$_2$ layer and substrate layer. According to elemental mapping analysis, it indicated that the TGO layer consists of Cr$_2$O$_3$ and mixed oxide (MO) was also observed beneath the TGO layer. The thickness of the MO layer in two-stage thicker than in a single stage of the coating sample. The growth of MO caused a detrimental effect mainly in the interface layer and it occurred due to a small initial porosity in the two-stage coating sample [9]. A small porosity influenced lowering the resistance of the topcoat layer, thus MO layer increased [10].

This result was also verified by elemental line analysis (Figure 4) where Cr element from the substrate of Inconel 625 diffused outward and reacted with the oxygen during sintering proses and formed Mixed Oxide (MO) that are Cr$_2$O$_3$ oxide and NiO. It is shown that the diffusion layer having well bonded with the substrate and the thickness of the diffusion layer was about 4 – 6 µm. The growth of MO quicker than the growth of a protective layer of α-Al$_2$O$_3$ with a nearly linear curve [10]. In the coating sample, aluminum from the substrate is low (0.4 %) and another element contained 0.9 wt%, consequently, α-Al$_2$O$_3$ was hardly formed and promote the formation of MO.
Figure 3. A cross-sectional microstructure and its elemental mapping analysis of Fe$_2$O$_3$ doped 3YSZ coating after sintering at a temperature of 1200 °C for 4 h: (a) two-stage and (b) single stage of voltage treatment.

Figure 4. Elemental line analysis of Fe$_2$O$_3$ doped YSZ coating after sintering at a temperature of 1200 °C for 4h: (a) two-stage and (b) single stage of voltage treatment.
3.2. Mechanical properties

Figure 5 shows microhardness measurements of Fe$_2$O$_3$ doped YSZ coating. It was measured that the surface hardness of YSZ ceramic coating with two-stage voltage treatment is higher of 28.64 HV than the sample developed by a single stage of voltage treatment. The hardness results have corresponded with the surface structure of a two-stage coating sample which having low porosity [11]. The two-stage can counterbalance the increasing resistance of deposit. The rate of particle accumulation can be solved at a constant and moderate value, it would result in a uniform and dense microstructure [7].

![Figure 5](image5.png)

**Figure 5.** Micro hardness measurements of Fe$_2$O$_3$ doped YSZ coating after sintering at a temperature of 1200 °C for 4h.

3.3. X-Ray diffraction

Figure 6 shows the XRD spectra obtained from the commercial of 3YSZ powder, green body, and coating sample after sintering at a temperature of 1200 °C for 4h. It indicated the transformation from tetragonal to monoclinic crystal structure in the ZrO$_2$ phase before (as 3 YSZ powder) and after (as the green body) EPD processes. This results due to the martensitic phase transformation from ZrO$_2$ tetragonal metastable to monoclinic was probably induced by the fracture of YSZ particles during homogenizer and sonication. The phase transformation is also influenced by low content of yttria stabilizer [12]. Sintering treatment might promote the decrement of volume fraction in monoclinic structure and transform to tetragonal crystal structure. This shows that ZrO$_2$ can be stabilized by Fe$_2$O$_3$ dopants, based on chemical reactions below:

$$2Fe_2O_3 \xrightarrow{ZrO_2} 3Fe'_2Zr + Fe''_2 + 6O_0^X$$

This indicates that no additional oxygen vacancies were produced after adding Fe$_2$O$_3$ to 3YSZ [13].

![Figure 6](image6.png)

**Figure 6.** XRD spectra: commercial of 3YSZ powder, green body and coating sampel after sintering at a temperature of 1200 °C for 4h.
4. Conclusion
The microstructure and mechanical hardness of Fe₂O₃ doped YSZ coating produced by electrophoretic deposition at single- and two-stage voltage treatments on Inconel 625 substrate has been investigated. The coating produced by two-stage voltage treatment was less porous than that of resulting from single-stage one. As a consequence, the hardness was 28.64 HV higher than the coating developed by a single stage of voltage treatment. A protective oxide scale was homogenously deposited on both coatings which indicated the good performance of the coatings. The major phase detected in the coating was ZrO₂ with a tetragonal crystal structure. The tetragonal structure which is very essential for the thermal barrier coating system applications was successfully stabilized by the addition of a small amount Fe₂O₃.

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