Improvement of erosion resistance of alumina-phosphate ceramic coating on mild steel by SiC addition

D Idamayanti¹, I L Nurhakim¹, B Bandanadjaja¹, W Purwadi¹, N Lilansa²
¹ Foundry Engineering Department, Politeknik Manufaktur Bandung, Jl. Kanayakan no. 21 Bandung, Indonesia
² Automation Engineering Department, Politeknik Manufaktur Bandung, Jl. Kanayakan no. 21 Bandung, Indonesia

E-mail : idamayanti79@gmail.com

Abstract. This research is focused on the application of the Al₂O₃-phosphate ceramic coating on mild steel surface to protect mild steel from erosion in coal dust environment. Erosion resistance of mild steel could be improved by overlay it with SiC in the Al₂O₃-phosphate ceramic coating. As a filler, Al₂O₃ was mixed with 20%, 40%, and 60% SiC by using aluminium phosphate as a binder and heated at 220 °C for 5 hours. X-ray diffraction testing was conducted to observe the phase of Al₂O₃-SiC phosphate ceramic coating. Meanwhile, surface morphology and adhesion characteristic of Al₂O₃-SiC phosphate ceramic coating were analyzed by scanning electron microscope. To analyze the erosion resistance quantitatively solid particle impingement test by applying gas jets at the right angle (90°) against a sample surface has been conducted. The results showed that Al₂O₃-SiC phosphate ceramic coating is strongly bound to the mild steel surface without the presence of any void. The higher the SiC content can increase the ceramic coating density and its erosion resistance. The SiC 60% produces four times higher erosion resistance than uncoated mild steel. The material characterization of Al₂O₃-SiC phosphate ceramic coating proves that SiC gives a significant impact on the enhancement of erosion resistance of the Al₂O₃-SiC phosphate ceramic coating.

1. Introduction
The purpose of this research is to improve the resistance of the inner cone of a coal pulverizer against the erosion. The inner cone as shown in figure 1 is part of the coal pulverizer. When observed it has erosion failure due to coal dust scouring. The inner cone itself which generally made of mild steel serves to direct the coal dust to the classifier, therefore, it should show excellent resistance against erosion caused by the flow of the coal dust. The mild steel is widely used as a structural material in some of the engineering applications due to its good machinability, high thermal conductivity, and superior mechanical strength [1].

Nevertheless, this material is highly affected by corrosion and wear and last consequently shorter service life. Applying ceramic coating on the surface of the mild steel is one of the most reliable erosion protection methods. Ceramic coatings are widely applied to protect some metal or cement machine components in power and refractory industries against chemical corrosion, abrasive wear, and high-temperature oxidation environments [2,3].

The ceramic coating consists mainly of oxide particles such as Al₂O₃ (mostly used), CaO, MgO, Cr₂O₃, etc., and binder. Several types of binder can be applied for ceramic coatings such as polymers, inorganic materials, and chemically bonded ceramic. Polymeric binder includes polyvinyl alcohol, Teflon, and acrylic [4] in the most cases cannot withstand against high temperature above 200 °C, while the inorganic binders namely sodium silicate, and hydraulic cement show high strength at the room temperature but less resistant at elevated temperature [5]. Type
of binder used plays important roles in binding ceramic coating adhering to the substrate. The binder does not only
adhere between the coating to the metal surface but also binds the ceramic particles together so that the ceramic
particles is not peeled off the coating [3]. An additional challenge applies to binders for making alumina ceramic
coating that operates at high temperatures. According to previous studies by the authors, aluminium phosphate
is preferred as a refractory and alumina ceramic coating binder due to its high strength, high-temperature stability,
abrasion resistance [1,6,7], good adhesion, and reduced risk of cracking under high heating rate after curing [8].

![Figure 1. The failure of inner cone coal mill pulverizer.](image)

Also, the aluminium phosphate binder also presents other interesting properties, such as excellent mechanical properties, low-cost preparation, short setting time and low-temperature ceramic “sol-gel like” coating which can be applied below 250°C [6,8]. The phosphate binder is firstly synthesized by reacting aluminium hydroxide and phosphoric acid to form monoaluminium phosphate (MAP). Subsequently, the MAP is mixed with ceramic particles such as alumina, magnesia, and zirconia to result in a ceramic slurry system which is known as chemically bonded phosphate ceramics (CBPC) [9]. Many researchers have observed CBPC and applied on metals to enhance corrosion and abrasion resistance of metals [1–3,6,10]. They modified a kind of ceramic materials to improve the mechanical properties of the phosphate bonded Al₂O₃ ceramic coating. He et al [5] has investigated the effect of SiC in the Al₂O₃-phosphate ceramic coating. It showed the improvement of wear rate of phosphate bonded Al₂O₃-SiC ceramic coating due to the increasing of SiC content. This phenomenon is very logical due to the high hardness of SiC particles compared to Al₂O₃ particles [11]. This research has been conducted to investigate the effect of SiC addition in phosphate bonded Al₂O₃ ceramic coatings as abrasive ceramic particles to enhance the erosion resistance of coated mild steel as representative materials for pulverizer inner cone. The SiC particles were mixed with Al₂O₃ to form ceramic slurry using monoaluminium phosphate as a binder. The performance of phosphate bonded Al₂O₃-SiC ceramic coating on the mild steel was tested by alumina particle impingement using gas jets at the right angle (90°) against a specimen surface and was then verified by surface morphology using a scanning electron microscope. The gas jet containing alumina particles is applied to simulate the real condition. The results can optionally be taken for increasing the life of the inner cone pulverizer.

2. Experimental Work

2.1. Raw materials and specimen
The materials which are used for phosphate bonded Al₂O₃-SiC ceramic coating were alumina (Al₂O₃) as a ceramic particle, SiC as a filler of ceramic system, and Al(OH)₃ – H₃PO₄ as raw materials of the monoaluminium phosphate (MAP) binder. Alumina (Al₂O₃) size was 50 – 60 µm with round shapes, obtained as technical grade material. The particle size of SiC was average of 126,36 µm with irregular shapes. Both Al₂O₃ and SiC have different particles morphology as shown in figure 2. Phosphoric acid (85%), aluminium hydroxide (Al(OH)₃), methanol and aquadest were used as technical grade material
without further purification. The specimen used in the experiment was mild steel with 5 mm thickness. The chemical composition is listed in table 1. The specimen was cut to a size of 25 mm x 25 mm for implementing the ceramic coating. Furthermore, the specimen was cleaned by methanol to remove scale, corrosion, and other contaminants.

Table 1. Chemical composition of specimen.

| C (%) | Si (%) | S (%) | P (%) | Mn (%) | Ni (%) | Cr (%) | Mo (%) | Cu (%) | Fe (%) |
|-------|--------|-------|-------|--------|--------|--------|--------|--------|--------|
| 0.05  | 0.01   | 0.006 | 0.01  | 0.30   | 0.005  | 0.01   | 0.003  | 0.01   | 99.54  |

Figure 2. The particles morphology of Al$_2$O$_3$ (a) and SiC (b).

2.2. Synthesis of monoaluminium phosphate binder (MAP)
Monoaluminium phosphate (MAP) as a binder was synthesized by reaction of phosphoric acid (H$_3$PO$_4$) and aluminium oxide [5]. The reaction between phosphoric acid and aluminium hydroxide was carried out in deionized water at an Al/P (1/3) molar ratio. The mixture was stirred for 15 minutes at 100 °C to form MAP. Subsequently, the reaction product was dried at ambient temperature and was characterized by X-Ray Diffraction (Rigaku SmartLab X-Ray Diffractometer). The design of the MAP molar ratio refers to the stoichiometry reaction that follows the equation (1).

$$3H_3PO_4 + Al(OH)_3 \rightarrow Al(H_2PO_4)_3 + 3H_2O$$ (1)

The density of the MAP was measured using pycnometer to control its viscosity for coating application.

2.3. The formation of phosphate bonded Al$_2$O$_3$-SiC ceramic coating on mild steel
Recently, phosphate bonded Al$_2$O$_3$-SiC ceramic coating is widely used because the process can be carried out at room temperature, easy to apply and low-cost process [10]. It was applied to the prepared mild steel using the brushing technique. To produce the Al$_2$O$_3$-SiC ceramic suspension, the MAP binder was slowly stirred with Al$_2$O$_3$-SiC particles at a ratio of 1:1. The various amount of SiC in the Al$_2$O$_3$-SiC system studied were 20%, 40%, and 60%, respectively. He et al [5] and Chen et al [3] used SiC as an abrasive material to improve the mechanical properties of the Al$_2$O$_3$ phosphate ceramic coating. Phosphate bonded Al$_2$O$_3$-SiC that coated on the mild steel was hardened by following heat treatment processes:

Phosphate bonded Al$_2$O$_3$-SiC ceramic coating on the mild steel was dried at ambient temperature to evaporate water content for two hours. The heat treatment of phosphate bonded Al$_2$O$_3$-SiC ceramic coating was continued at 80 °C for 2 hours, then was held at 220 °C for 5 hours to obtain the berlinite phase.
2.4. Characterization of phosphate bonded \( \text{Al}_2\text{O}_3\text{-SiC} \) ceramic coating

This research involved some instruments for the characterization process. Optical Emission Spectrometer (Spektris ARL 3460) was used to analyze the chemical composition of mild steel. Macroscopic observation of phosphate bonded \( \text{Al}_2\text{O}_3\text{-SiC} \) ceramic coating was done by using the optical microscope (Olympus). Scanning Electron Microscope (Hitachi SU3500) was used to observe the surface morphology of the ceramic coating and its binding strength on the mild steel and the measuring of alumina or SiC particles size. Erosion characteristic of the mild steel and ceramic coatings were observed using SEM magnification at 200x. X-Ray Diffraction (Rigaku SmartLab Diffractometer) were carried out to observed phase identification of the binder and ceramic coating. Diamond cutting saw was used to a cross-sectional cutting of the ceramic coating. Erosion tester (Ducom triboinovator) was used to examine the erosion resistance of the ceramic coating according to ASTM G76-02 (standard test method for conducting erosion test by solid particle impingement using gas jets). The velocity of the testing is 30 m/s up to 70 m/s for 10 minutes with an impact angle at 90°. The solid particles selected were alumina particles close to the real conditions in coal dust environment. The erosion resistance according to erosion rate (mg/Kg) and was measured as weight loss of the ceramic coating per weight of the erodent material (alumina).

3. Result and Analysis

3.1. Characterization of synthesized monoaluminium phosphate binder (MAP)

MAP binder has been successfully fabricated with its density of 1.71 g/cm\(^3\) as much as resulted by He et al [5] for ceramic coating application. According to XRD patterns in figure 3, there is a mixture of several phases, namely aluminium hydrogen phosphate (known as a MAP) and aluminium hydrogen phosphate hydrate (known as MAP monohydrate). The intensity of the MAP as a function of its content is almost proportional to the intensity of MAP monohydrate. Chen et al observed initial dehydration of MAP trihydrate transforms to MAP as a dominant phase and MAP monohydrate as a secondary phase when the temperature is slightly elevated to 105 °C [3,5]. MAP binder plays an important role in binding between ceramic particles and also to bind the ceramic suspension to the mild steel surface. Chen et al [3] stated that MAP is the most effective bonding phase which fully formed when the temperature reaches 200 – 400 °C. A previous study concluded not only the concentration of MAP binder but also the reactivity and solubility of the selected oxide must be controlled during the processing steps to attain an improved bonding of the fine and coarse components [8].
3.2 Characterization of phosphate bonded Al$_2$O$_3$-SiC ceramic coating

Phosphate bonded alumina ceramic coatings are formed by slowly stirring alumina into a MAP binder solution. Alumina is a kind of amphoteric oxide that may slowly dissolve in aqueous MAP binder being weakly basic cation with small radii for the formation of cold-setting ceramics known as a kind of chemically bonded phosphate ceramics (CBPCs). The kinetics of formation CBPCs are the dissolution of alumina, the formation of aquosols by hydrolyzes, acid-base reaction and condensation into a CBPC, percolation and gel formation, saturation then the formation of crystallization into a monolithic solid of CBPC. Thus, unreacted alumina is available to form a good stable ceramic [12]. In this work, the addition of SiC in the Al$_2$O$_3$ ceramic system acts as a filler which enhances the mechanical properties of CBPC such as wear resistance, erosion resistance, and corrosion resistance [3,5]. The XRD patterns in Figure 4 show the composition of phosphate bonded Al$_2$O$_3$-SiC ceramic coating. The XRD peaks reveal the phases of residual aluminium oxide (Al$_2$O$_3$), berlinite, and cristobalite. The reaction of alumina particles and MAP binder produced aluminium phosphate (AlPO$_4$). As explained by Morris et al [13], AlPO$_4$ comes up as berlinite, tridymite cristobalite forms. Fully formed berlinite is obtained by heating precipitated, amorphous, aluminium phosphate to 450 °C with lithium fluoride, but berlinite inversion, take place at lower temperatures (150 °C, [9]). Meanwhile, the cristobalite form can be obtained in the presence of sodium chloride as promoters of crystallization or temperature stability relationship of berlinite phase [13]. As shown in figure 4, AlPO$_4$ as cristobalite form is a dominant phase. Bandyopadhyay [14] stated that AlPO$_4$ as cristobalite might be formed when heated to 150 – 200°C.
Figure 4. XRD pattern of phosphate bonded Al₂O₃-SiC ceramic coating on the mild steel.

Berlinite (AlPO₄) is the target phase compound of phosphate bonded Al₂O₃-SiC on the mild steel which the kinetic transformation of berlinite is similar to the one in the conventional sol-gel process [12]. According to wagh et al [7] once aluminium oxide dissolves, it will form intermediate phase of AlH₃(PO₄)₂·H₂O which will react with remaining oxide (Al₂O₃) on the surface of their particle to form berlinite and bind them. The reaction may be written as the equation (2).

$$\text{Al}_2\text{O}_3 + 2\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O} \rightarrow 4\text{AlPO}_4 + 4\text{H}_2\text{O}$$ (2)

Wagh et al [15] predict that a very small amount of alumina must be converted to form the bonding phase. In the Al₂O₃-berlinite system, Al₂O₃ particles disperse due to alumina sol-cluster and the Al₂O₃ surface being highly electrostatically repulsive [16] and the product is mostly alumina with a thin coating of berlinite on the alumina [15]. In the case of the SiC-Al₂O₃ system, SiC particles absorb alumina sol-gel, resulting in a steric repulsive force between particles [16]. This phenomenon is essential to get complete dispersion of ceramic particle and preserve the final quality of the products. The solubility of alumina is very low (ΔH° = -837.8 kJ/mol) so that dissolution of alumina and its hydrate phases may be enhanced by elevating the temperature of the ceramic slurry. The heat treatment is also required for both drying and transforming crystalline and amorphous phases of aluminium phosphate [15].

| Oxides   | Reactions                          | ΔH (kJ/mol) |
|----------|-----------------------------------|-------------|
| Al₂O₃    | 2Al₂O₃ + H₃PO₄ → 2AlPO₄ + 3H₂O     | -45.75      |
| FeO      | FeO + H₃PO₄ → FeHPO₄·3H₂O         | -136.7      |
| Fe₂O₃    | 2Fe₂O₃ + 3H₃PO₄ → 2Fe(H₂PO₄)₃ + 3H₂O | -95.1       |

The ability to chemically bond Al₂O₃ and other ceramic particles like SiC on mild steel without complicated mild steel preparation are technologically important. Table 2 shows FeO or Fe₂O₃ as
corrosion products which commonly found on mild steel may easily react with MAP binder due to highly exothermic enthalpy value. Mechanical adhesion due to surface roughness is also possible [13], and this can be increased by elevated temperature.

Figure 5 illustrates that the Al₂O₃-SiC phosphate ceramic coating strongly adheres to the mild steel. Thus, a good interface bonding between the mild steel and ceramic coating is created. Along in the interface line, there is no void or other discontinuities. The thickness of the ceramic coating results in 352-460 μm.

![Figure 5. SEM Micrograph of the cross-section view of Al₂O₃-SiC phosphate ceramic coating on steel. (a) 20% SiC, (b) 40% SiC, (c) 60% SiC.](image)

3.3 Erosion resistance of phosphate bonded Al₂O₃-SiC ceramic coating

3.3.1 Effect ratio of SiC in the phosphate bonded Al₂O₃-SiC ceramic coating

The filler and its proportion in the compact affect both strength and thermal expansion [17]. Idamayanti et al [18] applied phosphate bonded Al₂O₃ ceramic coatings (without SiC) on mild steel, then the ceramic coating shows the erosion rate of 5mg/Kg. Unfortunately, the Al₂O₃ phosphate ceramic coatings absorb the humidity in ambient temperature and also disintegrated when placed in water [7,17,18]. Chen et al [3] fabricated Al₂O₃-SiC ceramic coating on A₃ steel which its wear durability is about two times that of uncoated A₃ steel. As mentioned above, SiC particle act both filler and ceramic slurry stabilizer due its steric repulsive force. Considerable porosity was found in the phosphate bonded Al₂O₃-20%SiC ceramic coating (as seen in Figure 7A) caused by the releasing of hydrates when berlinite formed [7] and also by rapid evaporation of excess water in the slurry [15]. 20 % SiC in the ceramic system does not affect significantly to make dense ceramic coating. Also, the increase of SiC content 40 % to 60% generates compact and homogenous ceramic coating (figure 8A and 9A). In this work, an erosion testing was conducted to measure the erosion resistance phosphate bonded Al₂O₃-SiC ceramic coating influenced by SiC content of 20%, 40%, and 40%, respectively, when compared to that of uncoated mild steel. Figure 6 shows that the erosion rate of mild steel is four times higher (20 mg/Kg) than the Al₂O₃-60% SiC phosphate ceramic coating (5 mg/kg).

These results show a relation between the hardness of material and erosion behavior (brittle or ductile) [19,20]. Mohs hardness scale of each material used is alumina of 9, SiC of 9-10, and berlinite of 6-7 [21]. According to the hardness levels, berlinite will erode first due to its the lowest hardness. When erodent materials impact both berline and Al₂O₃-SiC ceramic coatings, their resistance depends on the most prominent phase in the impacted area.
3.3.2 Erosion behavior of the Al$_2$O$_3$-SiC phosphate ceramic coatings

The erosion behavior of materials was affected by its bonding strength to face the solid particle impingement then accelerated by the impact angle. According to Hutchings et al [22], the erosion rate of ductile materials will be high at low impact angle (25-30°), while the erosion rate of brittle material will be high at high impact angle (90°). The phosphate bonded Al$_2$O$_3$-SiC ceramic coating as a kind of brittle material was tested at the high impact angle 90° to ensure its performance in severe erosion [19].

Figure 7-9 (B) shows the morphology after erosion testing. The surface morphology of phosphate bonded Al$_2$O$_3$-20%SiC ceramic coating releases a lot of debris that comes from berlinite peel off, then a lot of cavities are formed. The result is comparable to the morphology of phosphate bonded Al$_2$O$_3$-SiC ceramic coating developed by Chen et al [3]. Almost certainly, well-covered berlinite of Al$_2$O$_3$-60%SiC ceramic coating (figure 9B) is the most resistant toward particles impingement.

Figure 6. The effect of SiC addition on the erosion rate of phosphate bonded Al$_2$O$_3$-SiC ceramic coating.

Figure 7. SEM micrograph of the morphology of phosphate bonded Al$_2$O$_3$-20%SiC ceramic coating, before erosion testing (A), after erosion testing (B).
Figure 8. SEM micrograph of the morphology of phosphate bonded Al₂O₃-SiC ceramic coating before erosion testing (A), after erosion testing (B).

Figure 9. SEM micrograph of the morphology of phosphate bonded Al₂O₃-60%Si ceramic coating, before erosion testing (A), after erosion testing (B).

The higher the SiC content, the higher the particle density, the lower the porosity, and the lower debris releasing after erosion testing. The addition of 60% SiC in the Al₂O₃-SiC mixture showed the best performance against erosion.

4. Conclusion
A study of the SiC addition concerning the phosphate bonded Al₂O₃ ceramics system was carried out. It was found that SiC improves the erosion rate of phosphate bonded Al₂O₃-SiC ceramic coating. As high SiC was added in the ceramic coating, the erosion resistance of phosphate bonded Al₂O₃-SiC ceramic coatings increase. The addition of 60% SiC in the Al₂O₃-SiC ceramic coating produces four times erosion resistance if it compares respectively with uncoated mild steel. The Al₂O₃-SiC ceramic coating on mild steel results in good adhesion and produces 352-460 μm of the thickness.

References
[1] Ruhi G, Modi O P, Sinha A S K and Singh I B 2008 Corros. Sci. 50 639–49
[2] Lv F, Wang L and Wang E 2013 Adv. Mater. Res. 821–822 1256–60
[3] Chen D, He L and Shang S 2003 Mater. Sci. Eng. A 348 29–35
[4] Chung D D L 2003 J. Mater. Sci. 38 2785–91
[5] He L, Chen D and Shang S 2004 J. Mater. Sci. 39 4887–92
[6] Kamo L and Saad P 2005 Proceedings of WTC2005 World Tribology Congress III (ASME) 3–4
[7] Wagh A S 2004 Chemically Bonded Phosphate Ceramics (Elsevier Ltd)
[8] Luz A P, Oliveira G R, Gomes D T and Pandolfelli V C 2016 Ceram. Int. 42 8331–7
[9] Wagh A S 2013 ISRN Ceram. 2013
[10] Devapal D, Sebastain T V, Prabhakaran P V and Packirisamy S 2012 Mater. Sci. Forum 710 786–91
[11] Anon Mohs’ Hardness (Typical) of Abrasives
[12] Wagh A S and Jeong S Y 2003 J. Am. Ceram. Soc 86 1838–44
[13] Morris J H, Perkins P G, Rose A E A and Smith W E 1977 Chem. Soc. Rev. 2 173-195
[14] Bandyopadhyay K 1985 Phosphate Bonded Silicon Carbide Refractories (India: Indian Institute of Technology Kanpur)
[15] Wagh A S, Grover S and Jeong S Y 2003 J. Am. Ceram. Soc 86 1845–9
[16] Moorlag C 2000 Chemically Bonded Sol-Gel Ceramic: A Study of Alumina-Phosphate Reaction Products (Canada: University of British Columbia)
[17] Morris J H, Perkins P G, Rose A E A and Smith W E 1977 Chem. Soc. Rev. 6 173
[18] Idamayanti D, Ginanjar D, Bandanadjaja B, Purwadi W and Lilansa N 2018 Erosion behaviour of alumina ceramic coating on mild steel by the modified composition of phosphate binder International Seminar Material and Metallurgy (Tangerang)
[19] Ruff A W and Wiederhorn S M 1979 Treatise Mater. Sci. Technol. 16 69–126
[20] Levy A V and Chik P 1983 Wear 89 151–62
[21] Byrappa K, Prasad J S and Srikanthaswamy S 1986 J. Cryst. Growth 79 232–5
[22] Hutchings I M 1987 Wear by particulates Chem. Eng. Sci. 42 869–78

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