Influence of Sintering Temperature on Mechanical and Physical properties of Mill Scale based Bipolar Plates for PEMFC

Deni S. Khaerudin1,2, Rina Berliana1, Gatra B. Prakoso1, Dita R. Insyand1, Sagir Alva2

1 Fuel Cell Group, Research Center for Physics, Indonesian Institute of Sciences, Bld. 440 Kawasan Puspiptek Serpong, Tangerang Selatan 15314, Banten, Indonesia
2 Department of Mechanical Engineering, Universitas Mercu Buana, South Meruya No. 1, Jakarta 11650, Indonesia
deni.shidqi.khaerudini@lipi.go.id

Abstract. This work concerns the utilization of mill scale, a by-product of iron and steel formed during the hot rolling of steel, as a potential material for use as bipolar plates in proton exchange membrane fuel cells (PEMFCs). On the other hand, mill scale is considered a very rich in iron source having characteristic required such as for current collector in bipolar plate and would significantly contribute to lower the overall cost of PEMFC based fuel cell systems. In this study, the iron reach source of mill scale powder, after sieving of 150 mesh, was mechanically alloyed with the aluminium source containing 30 wt.% using a shaker mill for 3 h. The mixed powders were then pressed at 300 MPa and sintered at various temperatures of 400, 450 and 500 °C for 1 h under inert gas atmosphere. The structural changes of powder particles during mechanical alloying and after sintering were studied by x-ray diffractometry, scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX), microhardness measurement, and density – porosity analysis. The details of the performance variation of three different sintering conditions can be preliminary explained by the metallographic and crystallographic structure and phase analysis as well as sufficient mechanical strength of the sintered materials was presented in this report.

1. Introduction
Proton Exchange Membrane Fuel Cell (PEMFC) is one of the promising alternative energy technologies to be developed, because this technology has some advantages in term of high process efficiency, low operating temperature and producing electricity from electrochemical reactions in an environmentally friendly manner [1]. PEMFC consists of various components, among which bipolar plates allocate about 60 to 80% of PEMFC weight and 30 to 45% of their cost [2]. However, its use is not optimal yet, due to high weight and high production costs, which largely affected by bipolar plate.

Bipolar plate (BPP) is one the most significant part in PEMFC. The function of bipolar plate is the backbone of a PEMFC, facilitates water and thermal management, and provides conduits for reactant gases. Generally, there are two types of bipolar plate in PEMFCs; the carbon-based and the metal-based bipolar plate. The carbon-based bipolar plates have higher corrosion resistance and lower contact resistance, but they are considered as brittle and permeable to gases. Compared with the carbon-based bipolar plate, metal-based bipolar plates have higher mechanical strength, lower
permeability, and much superior manufacturability. Due to their high strength, metallic BPP can be made of very thin sheets with a thickness of 0.1 mm or less [3-6]. However, the main handicap of the metal-based bipolar plates is the lack of ability to combat corrosion in the harsh acidic and humid environment of PEMFCs.

The unique combinations of properties provided by aluminum and its alloys make aluminum one of the most versatile, economical, and attractive metallic materials for a broad range of uses - from soft, highly ductile wrapping foil to the most demanding engineering applications. Aluminum alloys are the second after steels in use as structural metals. The applications of aluminum alloys are economical in many applications. These alloys, being formed by FeAl or FeAl ordered phases, are characterized by very good high-temperature corrosion resistance in oxidizing and sulphidizing environments together with low cost of the constituents and lower density (5.7 g cm$^{-3}$ for FeAl). Possible production routes of iron aluminides concern casting technology, hot working, or powder metallurgy processes. Appropriately alloyed and treated, aluminum can resist corrosion by water, salt, and other environmental factors, and by a wide range of other chemical and physical agents [7-9]. Therefore, the alloy of aluminum and mill scale is ones of the metallic bipolar plates that can be considered, due to the possibility to mass production and decreasing PEMFC volume and weight, which lowers the overall manufacturing cost. As an alternative one, waste-based materials can also be utilized as raw materials, for instance, mill scale. Mill scale is a waste material from the steelmaking industry and considered has rich iron content (about 70-75% Fe). Thus, the high content of Fe in mill scale is potentially used as raw material for manufacturing metallic-based bipolar plate. In this study, in order to reduce the cost as well as utilize the industrial mill scale waste, we report a study of the utilization of mill scale based bipolar plate with some variation addition of waste of aluminum for evaluation and justification on their microstructural, physical and mechanical properties [10].

2. Experimental
In the present study, the industrial mill scale (as received from PT Krakatau Steel, Cilegon, Indonesia) the chemical composition (wt.%) of Fe total: 74.24%, Fe metal: 0.20%, Fe$_2$O$_3$: 52.02%, SiO: 0.25%. CaO: 0.97%, MgO: balance (analyzed by XPS), was chosen as raw material. After sieving of 150 mesh and to prepare the substrate sample, the waste of aluminum material was added—with a composition of 30%wt Al addition with temperature variations of 450, 475 and 500 °C. Thus, the blends were mechanically alloyed using a shaker mill in a discontinues milling manner with milling speed of 600 rpm, delay time of 20 minutes and total milling time of 3 h. To prepare the green body, the milled powders were pressed with a loading of 300 MPa at room temperature into the mould with diameter of 20 mm and targeted thickness of 3 mm. The green body was then sintered at those three variations sinter temperature for 1 h under inert gas atmosphere. After grinding and polishing, the samples obtained were microstructure analyzed by scanning electron microscopy (SEM Hitachi SU 3500) and with energy dispersive X-ray spectroscopy (EDX Horiba). Phase analysis was carried out by X-ray diffraction (XRD SmartLab, Rigaku) with a copper anode x-ray tube with 20 from 10 to 90° using a 0.01° step size and 0.20 second count time. To measure the hardness surface of sample, Vickers hardness was analyzed by Microhardness Tester (HV Leco LM100AT). The density and porosity analysis were carried out by Archimedes method.

3. Results and discussion
3.1. Phase characterization
The X-ray diffraction analysis was carried to identify the phases present in the powder of raw material and after the sintering process of alloyed sample, as showed in Figure 1. In this study, the bipolar plate samples were prepared by using the mill scale and 30 wt. % of aluminium. Mill scale is a waste material from the steelmaking industry and considered has rich iron content (about 70-75% Fe) and other oxide content. Therefore, the oxide phases that contained in mill scale can be observed due to the original of the raw mill scale content and during the heating process. Figure 1a shows the after milled
FeAl alloy powder for 3 h as well as their original raw materials of mill scale (Fe) and Al powder. From XRD peaks, it shows the existence of new phase Fe$_3$Al after 3 h milling process at 2θ value of about 65.899°. This Fe$_3$Al phase can be obtained due to some collision process between the ball milling (high-energy ball mills) and the powders during under the desired milling period and ball to powder ratio. Under such desired conditions, some eroded state of powder and size reduction will be occurred. Subsequently, the heat transfer of ball-powder process is also occurred due to the friction and collision, so that the new phase of Fe$_3$Al is formed.

Figure 1. X-ray diffractogram of (a) mill scale (Fe), Al and FeAl powder; and (b) FeAl sample sintered at 450, 475 dan 500 °C showing Fe$_3$O$_4$, Fe$_3$Al, FeAl and Al phases

Figure 1b shows the XRD peaks of the bipolar plate samples after sintered at different temperatures of 450, 475 and 500 °C. After the sintering process, the different phases can be observed, including Fe$_3$Al, Fe$_3$O$_4$ and FeAl phases. Generally, the sintering process is a heating process under the recrystallization temperature or melting point. In this study, the variation of sintering temperatures was carried out, however, the Fe$_3$Al phase can be detected and formed on each variation of sintering condition. When the sinter temperature increases, these phases are continuously transformed into FeAl and Fe$_3$Al phases. Fe$_3$Al phase was formed due to the influence of alloying process of mill scale,
which had sufficient Fe content, with the Al powder. In this case, the similar behaviour was observed i.e., the aluminium is melts; consequently the intermetallic Fe₃Al phase is emerged. The Fe₃Al phase has good mechanical and physical properties. Therefore, this material can be considered as a good raw material for bipolar plate purpose. From the XRD, after the sintering process, the magnetite Fe₃O₄ phase is also observed. This usually happened at high temperature. In this case, this occurs when the sintering temperature is increase, so that the Fe element (from the mill scale) tends to easily react with oxide that very reactive at high temperature condition. Other reason, the original content of mill scale itself, which contain some metal oxide as a by-product of the steel making industry. Therefore, the oxide phases that originally contained in the mill scale will be emerged during the sintering/heating process.

3.2. Vickers hardness

In this study, the hardness testing was carried out by Vickers micro-hardness method. This test was performed on the sintered samples in order to evaluate the Fe-Al bonding with respect of variations of sintering temperature of 450, 475 and 500 °C. The results showed that the obtained highest hardness value is 713.27 VHN for the sintered 475°C sample. From the graph, it also can be observed that the hardness value for two other different sintering temperatures at 450 and 500 °C are 421.79 and 384.26 HVN, respectively. At 500 °C, the hardness value shows decreases. This can be explained due to an over sintering condition which contributed by Al element. Another consideration is the pre-melting condition. This achieved when too high sinter condition on the necking process of the samples, then causing increases in porosity. Therefore, the pre-melting occurs so that the porosity increases at sinter condition of 500 °C. From the results, it is clearly indicated that the ideal sinter temperature should be less than 500 °C. From this study, the best one is at 475°C with hardness value of 713.27 VHN.

![Figure 2. Vickers Hardness results with different of sintering temperature at 450, 475 and 500 °C.]

3.3. Metallographic analysis

In this study, we further evaluated the microstructure of bipolar plate sample with the FE-SEM and EDX micrograph analysis, as shown in Figure 3. From the FE-SEM observation, from the surface view, indeed some void still can be observed. Further, indeed there are some inhomogeneous of the grain size, this can be explained due to the difference of melting point between the Fe (mill scale) and Al element. However, in term of hardness, as previously shown in Figure 2, the sintered 475°C is the highest one. This can be explained due to some better of Fe-Al compound bonding. Further, the point analysis is also indicated the existence of Fe₃O₄ and Fe₃Al phases, as also previously confirmed by XRD test result. However, one can be revealed from this observation is that the Fe₃Al phase is existed/overlapped on the surface of Fe₃O₄ phase.
Figure 3. FE-SEM metallography observation at x2000 magnification of FeAl sintered 475°C

Further analysis of EDX results are shown in Figure 4. One can be observed that the Fe and Al elements are distributed homogeneously from the sample surface. When the Fe₃Al phases are being produced by powder metallurgy process under desired reactive sintering condition, it can be expected that inter-diffusion of iron and aluminium will be occurred and the ordered phases will be formed after being heated to sufficient temperature. Simultaneously, the densifying of the material by sintering of powder particles would happen. FeAl₃ phase is formed by the Fe and Al solid state reaction below the melting temperature of aluminium. After that, the remaining aluminium element melt and are enriched by iron. Consequently, other Fe-Al phases precipitate from the melt [11].

Figure 4. FE-SEM and EDX of FeAl sintered 475°C
The wt.% results data from EDX analysis is also evaluated, as shown in the insert figure of EDX peaks. From the results, in here we focused on the Fe and Al elements. The observed Fe element is 44.7 wt.% and Al element is 17.0 wt.. After calculation, if we compared only between those two element, resulting on 72.4 wt.% Fe and 27.6 wt.% Al. Those results are relatively close with the designed alloying mixing sample of 70 wt.% mill scale (Fe) and 30 wt.% Al. This also indicated that the alloying process in this study is considered sufficient condition.

3.4. Density and Porosity Analysis

Figure 5 shows the density and porosity of Fe-Al samples. Figure 5a shows the density values with respect variation of sintering temperature. The obtained densities are 1.3495, 1.3793 and 1.3507 gr/cm³ at 450, 475, and 500 °C, respectively. The density value corresponds to the DOE standard for the bipolar plate material should be less than 5 gr/cm³. From Figure 5a, the density is decrease when the sinter temperature higher than 475°C. This can be explained due to effect of sintering temperature that causing some pre-melting phase when it’s over from their ideal sinter condition which contributed mainly from Al element in the study. The increasing of sinter temperature also causing some re-grain growth in the necking area that established during sintering. This initialized by re-diffusion of the elements due to the heat transfer effect which resulting in rearrangement of the grain interface in the necking area. This causes increasing on their porosity as a consequence decrease their density and mechanical properties of the bipolar plates sample. In Figure 5b, it can be seen clearly that the porosity is increase at sinter temperature of 500 °C, i.e. 1.0479 %. This value is inappropriate due to the DOE standard on the desired porosity which should be less than 1 %. Meanwhile, at 450 °C, the obtained porosity is 0.8374 % and at 475 °C is 0.7250 %; those two conditions are still considered the suitable condition due to the DOE standard value.

![Figure 5](image)

**Figure 5.** (a) Density and (b) Porosity of the bipolar plate sample after sintered at 450, 475 and 500°C

4. Conclusions

In this report, a series of sintered mill scale-based bipolar plate for PEMFC were developed by powder metallurgy method and the influence of various sintering condition on mechanical and physical properties were investigated. We fabricated it with aluminium addition of 30 wt.% and sintered at 450, 475 and 500 °C for 1h under inert gas atmosphere. The crystallographic analysis by XRD revealed that the obtained phases are magnetite (Fe₃O₄), Fe₃Al, FeAl and Al phases, while for the sintered sample the existence of aluminium (Al) phase is also can be detected. The hardness evaluation showed that the sample sintered 475 °C is much higher (713.27 VHN) than other two condition of sintered samples, as also confirmed by their density result (1.3793 g/cm³). This is tentatively distributed to the not optimum and over sinter condition of mill scale-aluminium element. The SEM micrograph and EDX analysis showed the inhomogeneous of grain size morphology of the sintered sample due to the
difference of optimum sintering condition of Fe and Al element. While the EDX analysis revealed the homogeneous distribution of Fe and Al element on the sample surface. The EDX analysis also confirmed the percentage of alloy composition that close to 70:30 wt.% of Fe:Al ratio. Those results suggest that the mill scale waste has some potential applications as bipolar plate that might be a suitable for commercialization of bipolar plate and PEMFCs technology after further research investigation and evaluation.

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