High-Temperature Oxidation Behavior of Fe-18Al Alloy Added with 2 %ZrO₂ Nanoparticles

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Abstract. The oxidation behaviour of ZrO₂ nanoparticles added to Fe-18Al alloy has been studied. Isothermal oxidation behaviour with various temperatures and times was investigated and the results of microstructure showed the presence of Fe₃Al intermetallic phases in grey color, Al₂O₃ oxide in white color, and the porosity indicated by dark color. The results of XRD and SEM-EDS analysis also confirmed the presence of the ZrO₂ nanoparticles in addition to Fe₃Al intermetallic phases and Al₂O₃ oxide phases. The addition of ZrO₂ nanoparticles tended to decrease oxidation rate by promoting Al₂O₃ layers.

Keywords: Isothermal oxidation, Oxidation rate, ZrO₂ nanoparticle, Al₂O₃ layer

1. Introduction

The processes that take place in various industries usually experience aggressive environments characterized by high-temperature and pressure, a large increase in temperature difference, large external stresses, the presence of oxidative and corrosive environment, and the presence of erosive foreign particles [1–4]. Such aggressive environments usually occur in propulsion and energy conversion engines like gas turbine engines, power plant boilers, steam turbines, oil refineries, and metal processing industries [5,6]. Hence, typical materials that are reliable to be used in such extreme conditions must have a combination between good physical and mechanical properties like a large melting point, high values of strength, toughness, creep resistance, thermal fatigue, and microstructure stability [7]. The application of the materials at high-temperatures tend to activate atoms which can precede the formation of new phases that are detrimental or increase the size of the reinforcing sediment particles which can cut down the effectiveness of fabrication [8,9].

The Fe-Al alloy has typical characteristic such as when the surface is oxidized in the alloy, it will form a thin protective layer [10]. In addition, the intermetallic phase of the Fe-Al alloy system falls into a group of materials that have high-temperature resistance and good creep resistance and possesses the mechanical properties which are beneficial when they are applied at high-temperatures. The alloy has a
good combination properties between physical and mechanical properties being relatively low-mass density, relatively high-melting point, high-temperature strength, good oxidation resistance, and good crack resistance [11–15]. Not surprisingly, the Fe-Al alloy becomes one of the choices of structural material suitable for high operating temperature and corrosive environmental applications [11,16].

The Fe-Al alloys can be processed through the mechanical alloying in which the Fe and Al feedstocks are in powder form or blended, milled and fractured forms [2,17–19]. The addition of certain elements or specific precursors like oxides nanoparticles for properties improvement of alloys is possible during the alloys preparation [10,20,21]. In this paper, we report the results of our current investigation on the additive effect of ZrO\textsubscript{2} nanoparticles during mechanically alloyed Fe and Al precursors to the oxidation behavior of Fe-Al alloys at temperatures 850 °C to 1050 °C.

2. Methods

Alloy samples were prepared from an analytical grade of Fe and Al powders with the sizes about 10 μm size. ZrO\textsubscript{2} nanoparticles of 30-60 nm and 99.99% purity were used as the additive during mechanical alloying of the Fe and Al feedstocks. The designated composition for the Fe-Al alloys were respectively Fe\textsubscript{82}Al\textsubscript{18} and Fe\textsubscript{80}Al\textsubscript{18}-(ZrO\textsubscript{2})\textsubscript{2} in weight percent (wt.%). The samples of such compositions were coded respectively F18 and F18Z2. The mechanical alloying process was carried out in a planetary ball mill, Mill PW 700i Toshiba operated under a rotating speed of 600 rpm, a vibration speed of 1270 Hz for 60-minute milling. The charge to ball mass ratio was 5:1 in a stainless cup of 285 ml capacity. The mechanically milled materials were charged into a cylindrical die and pressed under a compressive strength of 100 kg/cm\textsuperscript{2} using a hydraulic machine at the room temperature. The green compacts were then sintered in a ceramic tube furnace under a continuous argon gas flowing at a temperature of 1000 °C for 2 hours, followed by a furnace cooling to the room temperature. The oxidation process was carried out in a tube furnace at various oxidation temperatures of 850, 950, and 1050 °C for 1 hour and 4 hours holding time. All samples were furnace cooled to the room temperature. The oxidized samples were examined by an X-ray diffractometer for identification of the phase constitution of the oxide scales. The microstructure and the oxide composition of samples were observed under a scanning electron microscope (SEM) equipped with energy disperse X-ray spectrometers (EDX).

3. Results and Discussion

Figure 1 shows a weight of scale per unit area of sample F18Z2 compared with that of F18 after oxidation at various temperatures for 1 hr and 4 hrs. The plot represents the total mass of sample oxidized into scale. The total mass of the sample could be weighted because an increase in the amount of oxide layer on the surface took place without experiencing peeling. The plots clearly indicate that in both exposure times, the weight of scale per unit area formed in F18Z2 sample was less at any oxidation temperatures which confirm that the present of ZrO\textsubscript{2} nanoparticles in the samples had improved the high-temperature oxidation resistance. In addition, the results of the microstructure observations showed that Al\textsubscript{2}O\textsubscript{3} oxide was present in all samples, not exceptionally in the the ZrO\textsubscript{2} free sample. The difference between the two types of samples is that the amount of Al\textsubscript{2}O\textsubscript{3} oxide phase presented more in the ZrO\textsubscript{2} free sample. Meanwhile, the higher the oxidation temperatures, the grain of ZrO\textsubscript{2} free sample became coarser than that of the ZrO\textsubscript{2} added sample (see Figure 2.).
Figure 1. Oxidation kinetics Fe18 and Fe18Z2 a) for 1 hour, and b) for 4 hours

Figure 2. The microstructure of Fe18 and Fe18Z2 oxidized at various temperatures for a) 1 hour and b) 4 hours

The elements of the compounds formed in the sample were dominated by Fe, Al, Zr, and oxygen elements as shown by the SEM-EDX test results (see Figure 3). Fe elements will bond with Al to form intermetallic Fe₃Al compounds and the formation of Al₂O₃ protective layers by Al elements bond with oxygen gas. The occurrence of Al₂O₃ oxide as a protective layer on the surface will prevent oxygen gas to diffuse into the sample and bonds with Fe to form Fe₂O₃ or FeO oxides. Meanwhile, the presence of Zr as ZrO₂ nanoparticles will cover the porosity, so the oxygen gas cannot diffuse into the next layers. The results of XRD testing showed the formation of Fe₃Al intermetallic phases, Al₂O₃, and the presence of ZrO₂ nanoparticles as seen in Figure 4.

The oxidation process that occurs for 4 hours allows the Al₂O₃ oxide scale to exfoliate from the surface or oxide spalling. This process led the oxygen gas to diffuse and bind with α-Al or Fe₁₈Al intermetallic phases. E. Basuki, 2016 [1] explained that the oxidation process in metal alloys generally
takes place more complex because the elements present in the alloy have different affinity for oxygen and the different values of the oxides formation free energy. Therefore, the α-Al phase would bind to the oxygen gas firstly to form Al₂O₃ compared to the Fe₃Al intermetallic phases. This formation reaction corresponds to the XRD results of the sample with F18Z2 code which indicates the presence of Fe₃Al intermetallic phases besides Al₂O₃ oxide. Pavel Novak et al. [22] also reported that the formation of Al₂O₃ oxide at 800 °C would be the first than iron oxides (Fe₂O₃) because of the lower Gibbs energy of Al₂O₃ (-1778 kJ mol⁻¹ < -982 kJ mol⁻¹). This reason supports the process of formation of Al₂O₃ phase that would occur the first than the Fe₃Al intermetallic phases. The presence of ZrO₂ nanoparticles would promote the formation of Al₂O₃ oxide by covering the pores in the alloy so that α-Al would react with oxygen to form Al₂O₃ oxide. Therefore, the sample with F18Z2 code was more likely to form an Al₂O₃ oxide than iron oxide layer formation.

Figure 3. SEM-EDS micrograph for Fe18AlZ2 which was oxidized for 4 hours at 1050 °C

Figure 4. X-ray diffraction patterns for Fe18 and Fe18Z2 oxidized for 1 hour and 4 hours
4. Conclusion
In this study, the presence of $\alpha$-Al phase would bind with oxygen gas to form an $\text{Al}_2\text{O}_3$ oxide that functions as protective layers on the surface. The addition of $\text{ZrO}_2$ nanoparticles in the Fe-18Al alloys has improved the high-temperature oxidation resistance by covering the pores in the alloys that promoted the formation of $\text{Al}_2\text{O}_3$ oxide. The difference between the two types of alloys is that the amount of $\text{Al}_2\text{O}_3$ oxide phase was present more in the $\text{ZrO}_2$ free sample. Meanwhile, the higher the oxidation temperatures, the grain of $\text{ZrO}_2$ free sample became coarser than that of $\text{ZrO}_2$ added sample.

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Acknowledgments
The authors gratefully acknowledge the support of Postgraduate Program of Materials Science Universitas Indonesia for the research facilities. We are also thankful for the financial support provided by the Directorate of Research and Community Service Universitas Indonesia under program Grants of International Publication Indexed for Final Project Student 2018 (PITTA 2018 contract No. 2238/UN2.R3.1/HKP.05.00/2018.