The Porosity and Hardness of Fe-18Al Alloy Added ZrO$_2$ Nanoparticles

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Abstract. The additive effect of ZrO$_2$ nanoparticles in Fe-18Al based alloys through the mechanical alloying process to the porosity and hardness was investigated. Results of microstructure observations showed that the only intermetallic Fe$_3$Al present as the major phase in the samples along with other phases which are very minor together with the presence of porosity that indicated by objects of dark color. The porosity tends to diminish with the addition of ZrO$_2$ nanoparticles. However, the porosity is still visible on the Fe-Al alloy with the addition of 2% additive and the higher compaction load especially in the surface area. The results of phase study by XRD confirmed the presence of the intermetallic Fe$_3$Al. It is shown that ZrO$_2$ nanoparticles are dispersed in the metal matrix. The presence of ZrO$_2$ also confirmed by SEM-EDS. The fraction of pores that estimated based on the microstructure observation showed a decrease with an increase in volume fraction of ZrO$_2$ nanoparticles and the compaction load. The study concluded that the hardness of Fe-18Al alloys increased with a decrease in porosity which achieved in Fe-18Al alloy added with 2% ZrO$_2$ nanoparticles. The lowest porosity level is 0.17% and the highest hardness value is 352.59 HV.

Keywords: Mechanical alloying, Intermetallic, Nanoparticle ZrO$_2$, Fe-Al alloys, Porosity

1. Introduction
High temperature resistant alloys which meet specific needs characterized by a capability of able to be operated continuously without protection at temperatures above 1200°F (650°C) [1]. Metallurgically, such high temperature resistant alloys are characterized by high creep and oxidation resistances property [2]. The need for high temperature resistant alloys is now increasing, while the type of material that potential to have such specific properties is very limited. The limitation is due to high temperature operating conditions that require specific property to overcome the oxidation. So far, the best material, the so called super alloys are reliable to fulfil such requirement [1, 3, 4, 5]. Broadly speaking, there are three groups of metal alloys that can be used in high temperature applications respectively super alloys, refractory alloys, and intermetallic alloys [1, 6, 7]. However, the latter alloys are being attracted great
attention by many researchers because the alloys are technologically important to be produced at the reduced cost [8] [9].

One of intermetallic alloys which has good prospect for use at high temperature is iron-aluminium (Fe-Al) based alloys. Two types of intermetallic phase respectively Fe-Al (B2) and Fe3Al (D03) in Fe-Al based system has received widespread attentions which are expected that the intermetallic alloy can replace the stainless steels for high temperature applications. The alloy has a high temperature resistance through the formation of a thin layer on the surface when oxidized. The oxide thin layer protects the alloys which cause resistant to high temperature and good creep resistance coupled with reliable mechanical properties turning the alloy favourable for high temperature applications. It has been widely known that the Fe-Al alloys have a relatively low density, high melting point, possess a high strength property at high temperatures, good oxidation and crack resistances. Not surprisingly, the Fe-Al Alloy is one of the preferred materials applicable as the structural parts applied at high operating temperature with corrosive environment. [6, 10].

One of the fabrication process for the Fe-Al alloys are mechanical alloying in which powder of alloy components is milled, welded and fractured in a high energy ball milling apparatus and then subsequently annealed at sufficient temperatures, allowing the solid state reaction to take place for phase formation in the alloys. [11, 12, 13]. The alloy which produced from this process will have mechanical properties which still can be modified by the addition of tertiary metal oxides. Because of having a very high melting temperature and strength, the properties of alloys will improve. However, this process has drawbacks such as the porosity level that is high enough that will affect the alloy resistance to oxidation or the formation of an oxide layer and can reduce the mechanical properties, especially the strength of the material [14, 15, 16, 17, 18, 19, 20, 21].

In this paper, results of investigation on the hardness and porosity of Fe-Al alloys synthesized through mechanically alloying of the iron (Fe) and aluminium (Al) powders with the addition of 1 and 2 vol.% ZrO2 nanoparticles are presented and discussed. To study the microstructure and mechanical properties of the alloys, Scanning Electron Microscope, Vickers hardness testing was used. An additional tool an image analyser is used to evaluate the porosity in the alloys.

2. Experimental methods
Alloy samples were prepared from an analytical grade of Fe and Al powders. ZrO2 nanoparticles of 30-60 nm and 99.99% purity were used as during mechanical alloying the Fe and Al feedstock. The designated composition for the Fe-Al alloys are respectively Fe82Al18, Fe81Al18-ZrO2, and Fe80Al18-ZrO2 in weight percent (wt. %). Samples of such compositions are coded respectively F18, F18Z1 and F18Z2.

The mechanical alloying process was carried out in a planetary ball mill with a charge to ball mass ratio 5:1 in a stainless cup of 285 ml capacity. The ball was made of zirconium oxide with 10 mm in diameter. The planetary ball mill was operated under a jog speed maintained at a speed of 600 rpm for 60 and 90 minutes. The mechanically milled materials produced planetary ball milling was charged into a cylindrical die and pressed under a compressive strength of 90 and 100 kg/cm² using a hydraulic machine at room temperature. The green compacts were then sintered in a ceramic tube furnace with preheating temperature 200 °C for 30 minutes and then heated up to 1000 °C for 2 hours followed by a furnace cooling to room temperature.

Phase identification of all samples was characterized by XRD PANalytical Empyrean with an X’Pert MPD diffractometer (Cu Kα radiation, λ = 1.5406 Å, and generator settings 30 mA, 40 kV). The observation was carried out in the angle range 2θ = 20-80° and a step size of 0.017°. The microstructure of samples was observed under an optical microscope and SEM JEOL JSM-6360LA.
3. Results and discussion
Plot of XRD data for samples F18 and F18Z1 is compared in Figure 1. The identification study made to
the strong diffraction peak of the two plots suggest that the peaks are well matched with that of
intermetallic Fe₃Al phase referred to Jia Lia et al. [22]. Furthermore, when referring to the phase diagram
of Fe-Al system [16], composition of the two samples coded F18 and F18Z1 contained 18 wt.% Al must
be a single phase alloy with Fe₃Al phase the only phase in the samples. No other minor phases may be
identified confidently through their respective x-ray traces.

Hence, if other phases exist in the samples like Al₂O₃ in sample coded F18 and an additional minor
phase ZrO₂ in sample coded F18Z1, the fraction must be extremely small below the detection limit of
the x-ray diffractometer. The presence of Al₂O₃ is most probable since Al tends to oxidize when standing
alone and treated at a high temperature. While, the presence of ZrO₂ is also possible because the ZrO₂
component was added in the preparation of sample coded F18Z1. Fortunately, the additional of oxide
phase, especially Al₂O₃ is needed by material for high temperature applications as protective layers. U.
Prakash [9] reported that the sintering treatment of mechanically alloyed powders of Fe and Al changes
the crystal structure of α-Fe (ferrite) to an intermetallic Fe₃Al phase at high fraction of Al.

A set of photo images resulted from microstructure observation under an optical microscope is
presented in Figure 2. The images were taken in two different directions respectively surface section
and cross section. Samples are made of mechanically alloyed powder of two different milling time and
two different compaction loads. Basically, there is no difference in grain morphology of the two
directions indicating that the grains in the sample are equiaxed grain and randomly orientated. No prefer
orientation was observed in the samples.

The feature of the microstructure of the whole samples consisted of an intermetallic FeAl₃ as the
main phase appears dominantly in the whole area of observation, another phase α-Al₂O₃ was also
observed as the second phase. The microstructure of samples also shows small dark areas which
identified as the porosity. The porosity was found less in the ZrO₂ added Fe-Al samples and almost
porosity free as the fraction of additive increased to 2 % by weight. The compaction load seems gave
no significant improvement to reduce the porosity.

Figure 1. X-ray diffraction patterns of samples
coded (a) F18 and (b) F18Z1 after sintered at
1000°C for 2 hours
While SEM image for sample F18 is compared with that of F18Z1 in Figure 3 along with EDS spectrums of microanalysis. Porosity is clearly seen in the two types of samples. The present of ZrO$_2$ in the samples is also shown in the micrograph appear as fine particles. The particle was treated as the object for microanalysis. Result of EDS analysis to the spot on the surface of sample F18 shows that only Fe and Al are present with the weight fraction, respectively 87.67% and 12.33 % which close to the designated composition. Almost the same result of EDS analysis of the surface of sample F18Z1 was obtained, but with an additional energy peak of Zr which is assumed present as an oxide form of ZrO$_2$. The mass fraction of ZrO$_2$ is only 0.79 % closer to the designated composition in which the ZrO$_2$ was added 1 wt. %.

The formation of intermetallic Fe$_3$Al phase together with densification toward pore free samples were achieved through sintering at a temperature 1000 °C. The addition of ZrO$_2$ nanoparticles in sample coded F18Z1 is expected to enhance the hardness. Figure 4 presents result of image analysis for porosity in the samples ZrO$_2$ added Fe-Al samples compared with that of ZrO$_2$ free Fe-Al sample.
Images in Figure 4 confirm the suppression of pores in ZrO₂ added Fe-Al samples. The fraction of pores which originally 7.757 % in sample F18 was suppressed down to 2.641 % with the addition of 1 wt. % of ZrO₂ particles. Further suppression was achieved with the addition of 2 wt. % ZrO₂ particles. Results of porosity evaluation of the Fe-Al alloys as summarized in the Figure 4 confirmed that zirconia can minimize the porosity in the sample which prepared under consolidated the mechanically alloying powders. Hence, hardness of the sample can be expected is enhanced with the increase of zirconia content in the sample.
The ZrO$_2$ nanoparticles must be dispersed throughout grains of Fe$_3$Al in the sample to form a ceramic metal matrix composite. It is reasonable to expect the hardness of ZrO$_2$ added Fe-Al sample increases. The higher of the ZrO$_2$ content in the sample, the dimensions and the weight changes is down. Based on hardness data, the hardness value increases along with the increase of zirconia content in the sample. Supported by microstructural, and porosity calculation data as seen in figure 5.

4. Conclusion

In the light of the results and above discussion, it can be concluded that Fe$_3$Al phase is the only major phase of Fe-18Al alloys under studied. The other possible phases are suspected very minor present in the samples. The addition of ZrO$_2$ to the Fe-18Al alloys reduced the porosity from 7.757 % in the ZrO$_2$ free Fe-18Al sample to the lowest 0.53 % in the 2 wt.% ZrO$_2$ added Fe-18Al sample. Along with the diminishing of porosity, the hardness value of Fe-18Al based alloys increased from the lowest value of 160.38 HV to the high hardness value of 352.59 HV.
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