Microstructure and phase composition of Fe-B-Al coatings on low carbon steel prepared by using mechanical alloying technique

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Abstract. In the present study, varying composition of FeB-Al was coated on low carbon steel by using mechanical alloying technique for 4 hours and followed by heat treatment in vacuum atmosphere of 5.9 Pa at 700 °C. The microstructure and formed phases of FeB-50 at.% Al, FeB-25 at.% Al, FeB-12.5 at.% Al and FeB coatings were intensively discussed. The cross sectional observation indicates that the coating thickness tends to increase with increasing Al content. Before heat treatment, the coatings are composed of FeB and Al phases, depending on coating composition. After heat treatment, the intermetallic phases were identified. Interdiffusion layer was also formed in the FeB-50 at.% Al coating after heat treatment.

1. Introduction
Carbon steels have been widely applied for numerous structural and constructional applications due to its good mechanical properties, easy fabrication, and low production cost. In spite of that, this material is susceptible to damage at high temperature because of its poor oxidation resistance. Various studies have been attempted to improve the oxidation resistance of carbon steel. Generally, there are two main methods to enhance the oxidation resistance at high temperature, namely alloy enrichment and coating deposition. In some cases, the second approach is more preferable than the first one because coating deposition can improves corrosion, oxidation, and wear resistance of carbon steel and maintain mechanical properties of steels [1-3].

Aluminum (Al) is one of important elements to increase the corrosion and oxidation resistance of alloys and coatings due to the fact that it can act as reservoir for the formation of a thin, compact and adherent oxide film of Al2O3 on the surface of materials. This oxide scale plays a significant role to retard the diffusion of oxygen to the alloy substrates [3-4]. Previous study reported that in order to improve the oxidation resistance of steel, the deposition of a thin Al layer on the steel surface and its heat treatment were carried out to form a surface layer of iron-aluminum (Fe-Al) intermetallic compounds. These have much higher melting point than Al (about 650 °C) in combination with high oxidation resistance [5]. The surface layer of Fe-Al intermetallic compounds can also be formed by applying Fe-Al coating on the surface of low carbon steel and followed by heat treatment in argon atmosphere at 600 °C [1]. Implantation of boron ions into metals and alloys results a significant increase in surface microhardness. This approach becomes an alternative method for diamond coated...
tools [6]. However, there are limited studies on Fe-B-Al system as a coating. The preliminary investigation before material testing at high temperature is needed to gain a better understanding on coating characteristics as microstructure and phase composition of the coating. Coating uniformity and coating-substrate compatibility can be observed through the microstructure characterization whereas the informations of formed phase are useful to predict whether the coating tends to be protective. Eventually, acquiring characteristics of coating before high temperature oxidation test is essential for coating development.

The mechanical alloying (MA) technique is a novel and potential method for surface coating on metals and alloys because this technique allows thick coating to be formed in a short period of time at room temperature and in an ambient atmosphere with minimal surface preparation before deposition [7, 8]. The fundamental principle of this process is that the collisions of ball and powder on the surface of the substrate lead to powder particles trapped on the surface and get cold welded. This continuous and repeated processes result in deposition of coating powder on the substrate [3, 7, 8]. Fe-Al, Cr-Al, TiN and Ti-Al coatings had been successfully deposited on the substrate of low carbon steel, stainless steel and Ti by using MA technique [2, 3, 7, 8]. Nevertheless, there has been no report about deposition of Fe-B-Al coatings on the substrate of low carbon steel prepared by using MA technique.

Furthermore, the previous MA studies typically used high purity powders as the sources of coating materials. Investigation on ferro-alloy lumps as deposited materials is rare. Although, these materials are more accessible and inexpensive.

In this present study, we focus on the microstructure and the phase identification of Fe-B-Al coatings with varying composition on the substrate of low carbon steel prepared by MA and followed by heat treatment. Ferro-boron (FeB) alloy lumps is used to substitute high purity powders as the source of FeB materials.

2. Experimental Methods
The samples and coatings preparation procedures used in this study were similar to that explained in the previous works [3, 9]. The commercial low carbon steel was used as substrate. Based on X-ray diffraction pattern of the substrate (figure 1), it can be observed that the substrate is mainly composed by Fe. The steel plate was cut to rectangular specimens with a dimension of about 10 x 8 x 3 mm. Before coating, the surface of the specimen was polished mechanically using SiC papers for up to No. 1200 and ultrasonically cleaned in ethanol solution.

![Figure 1. X-Ray Diffraction Pattern of Substrate.](image)
In this recent work, for coating deposition, ferro boron (FeB) lumps and high purity (≥ 99%) Al powders were used as the starting materials. Chemical composition of FeB lumps is shown in table 1. FeB lumps were crushed into powders by using a high speed shaker mill for 2h. After FeB powder was prepared, FeB and Al powders with varying nominal compositions as 100FeB, 87.5FeB-12.5Al, 75FeB-25Al and 50FeB-50Al (in at%) were mixed for 1h with the ball to powder weight ratio of 5:1. The total mass of the powder in each composition was 10 grams. Then three low carbon steel specimens were put and charged into vial. This mechanical alloying process was undertaken for 4h in ambient air atmosphere. The collisions between balls and powder on the surface of carbon steel result in the deposition of coating powders on the surface of steel. The coated sample was then heat treated in vacuum of 5.9 Pa at temperature of 700°C for 1h. Afterwards, the specimens were cooled down inside the furnace chamber to room temperature.

| Table 1. Chemical composition of FeB lumps (wt.%) |
| C | Al | S | Si | P | B | Fe |
|---|---|---|---|---|---|---|
| 0.5 | 0.2 | 0.01 | 0.5 | 0.05 | 20 | Balance |

The observation of deposited coating was done by using Optical Microscope. X-Ray Diffractometer (XRD SmartLab Rigaku) with Cu Kα radiation at 40 kV and 30 mA was used to indentify the phase compositions of the coatings before and after heat treatment. The coating microstructure was observed by using Scanning Electron Microscope equipped with energy dispersive X-ray spectrometer (SEM Hitachi SU3500-EDX).

3. Results and Discussions

3.1. Coating observations by optical microscope

The micrographs of cross sectional deposited coatings observed by using an optical microscope are shown in figure 2. According to the results, FeB-Al coatings are successfully deposited on the surface of low carbon steel by using MA method. The thickness of the coatings depends on the composition of deposited materials. The coating with highest Al content (FeB-50 at.%Al) results the thickest coating layer.

![Figure 2](image)

**Figure 2.** Optical micrographs of the cross section (a) FeB, (b) FeB-12.5 at.%Al, (c) FeB-25 at.%Al and (d) FeB-50 at.%Al coatings on low carbon steel substrate.

3.2. Phase composition of the coatings

Figures 3(a) and 3(b) show the X-Ray diffraction patterns of FeB-Al coatings with various composition before and after heat treatment at 700 °C for 1h.

As shown in figure 3(a), X-ray diffraction analysis of FeB coating shows the diffraction peaks of Fe and FeB. Meanwhile, the diffraction peaks of Fe, FeB and Al are detected in the coatings with various Al content. The diffraction peaks of FeB are detected from the substrate while FeB and Al from the coating. The peak intensity of Al diffraction increases with increasing Al content. The XRD characterization results show that the intermetallic compounds were not formed.
As showed in figure 3(b), new phases are identified for each different coating composition after heat treatment. Peaks Fe$_2$B diffraction are observed in the FeB-0 at.%Al and FeB-12.5 at.%Al coating. The stable compound of Fe$_2$B will remain stable in the presence of iron at low and elevated temperature [10]. Intermetallic phase of AlB$_{10}$ is formed in the FeB-12.5 at.%Al coating while Fe$_2$AlB$_2$ intermetallic compound is formed in the FeB-25 at.%Al and FeB-50 at.%Al coating. The higher peak intensity indicates that crystal structure refinement was occurred during heat treatment.

### 3.3. Cross section micrograph of the coatings

The cross-sectional observation of the coating, before and after heat treatment at 700 °C was undertaken for FeB-50 at.%Al and FeB-12.5 at.%Al coating composition. The cross-sectional micrographs of FeB-50 at.%Al and FeB-12.5 at.%Al coatings are shown in figures 4 and 5, respectively. According to the cross-sectional SEM images, the thickness of FeB-50 at.%Al and FeB-12.5 at.%Al coatings are about 162 µm and 42 µm, respectively. It can be observed that higher composition of Al results thicker coating. This phenomena could be caused by the density of Al (2.7 g/cm$^3$) which is lower than the density of FeB (3.3 g/cm$^3$) so that in the similar mass, Al has higher volume than FeB. In this experiment, the total mass of all compositions are fixed. Therefore, coating with higher composition of Al has higher and results thicker coating. It also can be clearly observed that there is no crack at coating-substrate interface.

Based on the result of EDX point analysis, the light gray particles in the figure 4(a) are composed of FeB and the dark grey matrix is composed mainly of Al. It can be seen that before heat treatment, FeB particles are dispersed in the Al matrix. This means that the particles of Al and FeB are still coexist and do not form intermetallic phases. This result has a good agreement with XRD analysis.
which shows that mechanical alloying does not lead to the formation of intermetallic compounds. Grey particles, that are located on the surface of substrate, have bigger size than that are located near the surface of coating because particle size of coating powder decreases with increasing milling time while the coating layer on the surface of substrate is deposited in the earlier stage of milling.

![Cross-sectional micrographs of FeB-50 at.%Al coating on low carbon steel substrate](image)

**Figure 4.** Cross-sectional micrographs of FeB-50 at.%Al coating on low carbon steel substrate (a) before, (b) after heat treatment, (c) and (d) higher magnification of squared area in figure 4(b) and 4(c), respectively.

![Cross-sectional micrographs of FeB-12.5 at.%Al coating on low carbon steel substrate](image)

**Figure 5.** Cross-sectional micrographs of FeB-12.5 at.%Al coating on low carbon steel substrate (a) before and (b) after heat treatment.

Meanwhile, after heat treatment, three coating layers are observed on the substrate (figure 4(b)). According to the results of EDX analysis, Al elements predominantly compose the upper layer of the coating while Fe and B elements predominantly compose a layer below it. At the interface between FeB rich layer and substrate, there is interdiffusion layer which is composed mainly of Fe and Al elements. The formation of FeB rich and FeAl interdiffusion layers is attributed to Al element diffusion to the steel substrate. The thickness of Al rich, FeB rich and interdiffusion layers are around 106 µm, 32 µm and 24 µm, respectively.
Further detail characterization was carried out in the interdiffusion layer. At higher magnification, it can be observed that actually this layer consist of three different layers. The results of EDX point analysis at points 1, 2 and 3 shows that those three interdiffusion layers are consisted of 51.4 at.%Fe - 48.6 at.%Al; 28.6 at.%Fe - 71.4at.%Al; and 33.99at.%Fe – 66.01 at.%Al, respectively. The compositions are closed to atomic ratio of FeAl, Fe$_2$Al$_5$ and FeAl$_2$ intermetallic phases. This strongly suggests that intermetallic layers are formed in the layers number 1, 2 and 3, respectively (figure 4(d)). These intermetallic compounds cannot be identified by XRD analysis due to the fact that X-ray cannot penetrate to reach the interdiffusion area which is located around 138 µm in depth from the coating surface.

Although microstructure of FeB-12.5 at.%Al coating before heat treatment is quite similar with FeB-50 at.%Al coating, lower composition of Al leads to the formation of thinner coating (figure 5(a)). Meanwhile, after heat treatment, the interdiffusion layer, which is formed in the FeB-50 at.%Al coating composition, is not formed in the FeB-12.5 at.%Al coating composition. According to the EDX point analysis, the coating composition of around 39 µm in depth from surface is consisted of 7.69 at.% Al, 72.08 at.% B, and 20.23 at.% Fe. This coating composition is predicted to form AlB$_{10}$ intermetallic compound containing Fe which is also identified from XRD characterization.

4. Conclusion
Various composition of FeB-Al coatings are successfully deposited on the substrate of low carbon steel by using mechanical alloying technique followed by heat treatment. Mechanical alloying does not lead to the formation of intermetallic compounds. The microstructure and phase composition of FeB-Al coating depends on the composition of coating. Higher composition of Al in FeB-Al coating results thicker coating. Interdiffusion layer, which is composed of intermetallic phases, is formed in FeB-50 at.%Al coating after heat treatment.

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References
[1] Seidu S O and Kutelu B J 2013 J. Min. & Mat. Char. & Eng. 1 95-100
[2] Canakci A, Erdemir F, Varol T and Ozkaya S 2013 J. Powd. Tech. 247 24-9
[3] Sudiro T, Sebayang P, Aryanto D, Hia A I J and Sebayang K 2015 J. Tekn. Indonesia 38(3) 156-62
[4] Schweitzer P A 2007 Fundamentals of Metallic Corrosion: Atmospheric and Media Corrosion (Boca Raton: CRC Press) p 5
[5] Gellings P J 2005 Introduction to Corrosion Prevention and Control (Enschede: University of Twente Press) p 101
[6] Gogotsi Y G and Andrievski R A 1999 Materials Science of Carbides, Nitrides and Borides (Springer) p 270
[7] Romankov S, Komarov S V, Vdovichenko E, Hayasaka Y, Hayashi N, Kaloshkin S D and Kasai E 2009 Int. J. Metals & Hard Mat. 27 492-7
[8] Romankov S, Mamaeva A, Kaloshkin S D and Komarov S V 2007 Mat. Let. 61 5288-91
[9] Hia A I J, Sudiro T, Aryanto D and Sebayang K 2015 J. Phys. Conf.: Ser. 739 012131
[10] Lindsay T G and Tough G S 1985 Proc. Ist Conf. on Production Research (Nottingham) (New York: Springer) p 340