## High Temperature Oxidation and Corrosion of FeCrAlTiY-10 mass% MoSi<sub>2</sub> Coating on Low Carbon Steel Prepared by Spark Plasma Sintering Technique

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Abstract. In the present study, we prepared the FeCrAlTiY-10 mass%  $MoSi_2$  coating on low carbon steel using the spark plasma sintering (SPS) technique. Its resistance against oxidation and corrosion was studied in air and atmosphere containing 20 mass% NaCl at 700°C for 8 cycles. The results show that a dense coating layer is composed by (Fe,Cr) and  $MoSi_2$  phases. After high temperature oxidation test, a thin protective  $Al_2O_3$  layer was formed. While mix oxide scales composing of (Cr,Fe)<sub>2</sub>O<sub>3</sub>,  $Al_2O_3$ , and Fe<sub>3</sub>O<sub>4</sub> were formed after high temperature corrosion test. Althought, the affected area after corrosion test is more severe than after oxidation test, the corroded sample somehow has a lower mass gain compared to oxidized sample after 8 cycles exposure. This could be related to the effect of chlorine ions and oxide spallation during cyclic corrosion test.

Keywords: MoSi<sub>2</sub>, FeCrAlTiY, coating, carbon steel, spark plasma sintering, oxidation, corrosion

#### **INTRODUCTION**

Carbon steel metal material is widely used in many industries because it has several advantages, such as, high strength, good machining ability and low cost [1-2]. However, it has weaknesses on oxidation, corrosion and wear resistance, limiting its application under severe conditions. Accordingly, a protective coating is required for example to improve their oxidation and corrosion resistance.

MoSi<sub>2</sub> is a great attractive candidate material for the next generation high-temperature applications (600–1800°C) because it has high melting-point (2303 K), high strength and good thermal conductivity, relatively low density [3-6]. Therefore, it was considered for coating to protect the beneath materials from high temperature corrosion and oxidation. FeCrAITiY has been studied due to its resistance toward oxidation and corrosion at high temperature [7]. Modifying the coating or alloy material may lead the formation of a thin protective oxide scale.

Several studies have made efforts to improve the oxidation and corrosion resistance of materials by adding alloying elements and changing the coating methods in order to obtain maximum coating results. As a new kind of technology, spark plasma sintering (SPS) also known as pulsed electric current sintering (PECS) or field assisted sintering (FAST) has been proved to be applicable for synthesizing the metals, composites and ceramics under compressive pressure and continuous heating in vacuum. This technique has several advantages such as high efficiency, short sintering period, densification sintering, controllable coating thickness and a

relatively low temperature [8-9]. In addition, it is as a new method for coating fabrication with defined compositions and homogenous microstructures [10]. Beside that, SPS can prepare substances with high density [11].

In our previous work [12], we have studied the high temperature oxidation resistance of several compositions of flame sprayed FeCrAlTiY–x mass %  $MoSi_2$  (x = 0, 10, 20 and 30) coatings on carbon steel. We found that the presence of defects such as pores, gap and cracks in the coating becomes major factors in affecting the sample oxidation. In addition, during coating preparation the use of compressed air as gas carrier leads to oxidation of coating elements. The results of study indicated that the FeCrAlTiY-10 mass%  $MoSi_2$  coating showed a better oxidation resistance among the other coating composition. In order to improve the 10 mass%  $MoSi_2$  coating structure, a spark plasma sintering technique was used to prepare the coating on the surface of carbon steel. In this study, we also investigated its oxidation and corrosion behaviour in air and atmosphere containing 20 mass% NaCl, respectively. The results are presented and discussed in this paper.

#### **EXPERIMENTAL PROCEDURES**

Carbon steel namely ST 41 with a dimension of  $10 \text{mm} \times 10 \text{ mm} \times 3 \text{ mm}$  was used as substrate. All the samples were mechanically ground in various grit of abrasive SiC papers and then ultrasonically degreased in ethanol solution. Before coating preparation, the sand blasting process is carried out with a pressure of 12 bar to increase the strength of the substrat layer.

Two kinds of commercial powders were used in our study FeCrAlTiY-Sandvik Materials Technology Ltd. and MoSi<sub>2</sub>-Japan New Metals Co. Ltd. The FeCrAlTiY with 10mass% MoSi<sub>2</sub> content was selected as the coating composition. The carbon steel and powder coating were prepared in 20 mm of graphite dies. The substrate was burried with FeCrAlTiY-10 mass% MoSi<sub>2</sub> powder. Sebsequently, it was consolidated by a spark plasma sintering unit (DR. SINTER model SPS-625) at constant axial pressure of 30 MPa, heated from room temperature for up to 900°C in the evacuated chamber of less than 6 Pa.

After sample sintering and cleaning, the oxidation and corrosion resistance of the sample were studied in air and 20 mass% NaCl atmosphere at 700°C for 8 cycles by measuring the mass change of sample per unit area. The structure of 10 mass% MoSi<sub>2</sub> coating before and after high temperature oxidation and corrosion tests was analyzed using X-ray diffraction (XRD) and scanning electron microscope (SEM) attached with an energy dispersive X-ray spectrometer (EDX).

#### Phase Composition and Microstructure of FeCrAlTiY-10 mass% MoSi2 Coating

Fig.1(a) shows the XRD pattern of FeCrAlTiY-10 mass% MoSi<sub>2</sub> coating deposited using Spark Plasma Sintering (SPS) technique on the surface of low carbon steel. The diffraction peaks of FeCrAlTiY-10 mass% MoSi<sub>2</sub> coating are detected as (Fe,Cr) and MoSi<sub>2</sub> phases. There is no oxide formed due to that the sintering process with SPS is carried out in a vacum condition (< 6 Pa), hindering the oxidation of coating elements. Fig. 1(b) shows cross-sectional microstructure at the coating/substrate interface. It can be seen that a small fraction of pore can be observed.



FIGURE 1. (a) XRD patterns and (b) SE-SEM cross-sectional microstructures of FeCrAlTiY-10 mass% MoSi2 coating

Fig. 2 show the EDX element mapping of FeCrAlTiY-MoSi<sub>2</sub> coating after sintering at 900°C. The results show that the dominant coating elements are Fe (magenta color intensity), Cr (cyan color intensity), Mo (pink color intensity) and Si (red color intensity). No oxygen distribution is found in Fig. 2. This indicates that the

oxidation during coating preparation does not occur. The detection of Fe, Cr, Mo, Si distribution in the coating supports the XRD analysis results which show that the coating is composed of (Fe,Cr) and  $MoSi_2$  phases, as shown in Figure 1(a)



FIGURE 2. Corresponding EDX elemental mapping of FeCrAlTiY-10 mass% MoSi2 coating

#### **Oxidation and Corrosion Kinetic**

Figure 3 shows the mass gain curve per unit area of FeCrAlTiY coating with 10 mass%  $MoSi_2$  after oxidation and corrosion test at 700°C for 8 cycles. In the preheating stage, oxidation at high temperatures cause a rapid surface reaction which cause an increase in the rate of ion migration, resulting in the oxide layer formation [13] and an increase in mass gain of the sample. As shown in Fig. 3, the corroded sample has a lower mass gain compared to oxidized sample at 700°C for 8 cycles which is 0.029 mg/mm<sup>2</sup> and 0.237 mg/mm<sup>2</sup>, respectively. It is interesting to note that for corroded sample, the mass gain increases in the first cycle of the test then decreases with the increase of cyclic corrosion time. This is probably due to the influence of cloride ions. In the atmospheric condition, chloride ions seem to only work during the corrosion initiation and failed to penetrate through the thick rust layer at later stages, so that corrosion rates increased initially and then declined with the exposure time in atmosphere [14]. In addition, some amount of corrosion products may spall out from the sample surface.



FIGURE 3. Mass gain curves of FeCrAlTiY coatings with 10 mass% MoSi<sub>2</sub> after oxidation and corrosion test at 700°C for 8 cycles

#### Phase Composition and Microstructure of Low Carbon Steel After Oxidation and Corrosion Test

Fig. 4(a) shows the results of XRD analysis of FeCrAlTiY-10 mass%  $MoSi_2$  coating after oxidation test at 700°C for 8 cycles. The results show that 3 phases namely (Fe,Cr),  $MoSi_2$  and  $Al_2O_3$  are confirmed from the sample reflection, suggesting that the oxidation product of this coating is mainly an  $Al_2O_3$ .



FIGURE 4.(a) XRD patterns and (b) SE-SEM cross-sectional microstructures of FeCrAITiY-10 mass% MoSi<sub>2</sub> coating after oxidation test at 700°C for 8 cycles

The cross-sectional microstructures of the coating after high temperature oxidation test are given in Fig 4(b). Visually, no significance different is found in the coating after and before oxidation test (Fig. 1(b)). However, EDX elemental maps of oxidized sample as shown in Fig. 5 clearly show the fine distribution of Al and O in the external layer. This result is in good agreement with the result of XRD analysis, as shown in Figure 4(a) which is confirming that the fine distribution of Al and O must be  $Al_2O_3$  layer. This thin oxide layer can acts as protective barrier for oxygen inward diffusion.



FIGURE 5. Corresponding EDX elemental mappingof FeCrAITiY-10mass% MoSi<sub>2</sub> coating after oxidation test at 700°C for 8 cycles

Figures 6 (a) and (b) show the XRD pattern and typical SE-SEM cross-sectional microstructure of FeCrAlTiY-MoSi<sub>2</sub> coating on low carbon steel after corrosion test in air at 700°C for 8 cycles, respectively. As shown in Fig. 6(a), the peaks reflection after high temperature corrosion test correspond to (Fe,Cr), (Cr,Fe)<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub>,



FIGURE 6. (a) XRD patterns and (b) SE-SEM cross-sectional microstructures of FeCrAlTiY-10 mass% MoSi<sub>2</sub> coating after corrosion test at 700°C for 8 cycles

Fig. 7 shows the result of EDX element mapping of FeCrAITiY-10 mass%  $MoSi_2$  coating after corrosion test. The magenta, cyan, pink, red, blue and green color intensities correspond to Fe, Cr, Mo, Si, Al and O distribution, respectively. The EDX elemental maps clearly indicate the distribution of Fe, Cr, Al and O on the coating surface. This results supports the XRD analysis which determine the corrosion products composing of (Cr,Fe)<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> as shown in Figure 6(a).



FIGURE 7. Corresponding EDX elemental mapping of FeCrAlTiY-10mass% MoSi<sub>2</sub> coating after corrosion test at 700°C for 8 cycles

In general, the chlorine attack leads to the formation metal chlorides that may be in the form of gas at high temperatures, resulting in weight loss. It can act as a catalyst for material deterioration and is often not easy to be observed due to its volatile nature. The volatile species of chlorides results in the development of cracks and pits, which provide easy path for the species to penetrate into the alloys [15]. This may be the reason why the detached area of corroded sample is severe compared to oxidized sample.

#### CONCLUSIONS

- 1. The SPS method significantly suppress the coating element oxidation during sample preparation.
- 2. The FeCrAlTiY–10mass% MoSi<sub>2</sub> coatings prepared by SPS technique effectively improves the resistance of carbon steel toward oxidation and corrosion at high temperature.

- 3. After oxidation test, a thin Al<sub>2</sub>O<sub>3</sub> scale was formed on the coating surface, leading to high protection from environmental degradation.
- 4. The presence of chlorine containing atmosphere promotes the mixed oxide formation consisting of (Cr,Fe)<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub>, resulting in less protection to the environmental degradation.

#### ACKNOWLEDGEMENT

The authors thank Mr. Ciswandi and Mr. Edi Setiawan for technical support and discussion. The authors also acknowledge Research Center for Physics-Indonesian Institute of Sciences for providing characterization facilities. This work is partially supported by Program Unggulan 2018 of Indonesian Institute of Sciences.

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## The Effects of MoSi<sub>2</sub> Addition on High Temperature Oxidation Behavior of Flame Sprayed FeCrAlTiY Coatings

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**Abstract** - The FeCrAlTiY coatings containing 0, 10, 20 and 30 mass% MoSi<sub>2</sub> were developed using a flame spray technique on the surface of low carbon steel. The effect of MoSi<sub>2</sub> addition on the structure and high temperature cyclic oxidation resistance of FeCrAlTiY coatings was investigated at 700°C for up to 8 cyclic times. The results show that the FeCrAlTiY-MoSi<sub>2</sub> flame spray coatings contain oxides, pores, fully and partially melted particles. As the MoSi<sub>2</sub> content increases, the coating tends to become more porous. After 8 cycles exposure at 700°C, the 10 mass% MoSi<sub>2</sub> addition to FeCrAlTiY coatings exhibits effective protection for carbon steel toward oxidation at high temperature. While, 20 and 30 mass% MoSi<sub>2</sub> additions show a deleterious effect in oxidation resistance of FeCrAlTiY coatings. The details and analysis of results obtained were presented in this paper.

Keywords: Flame spray, MoSi<sub>2</sub>, FeCrAlTiY, coating, structure, oxidation

#### 1. INTRODUCTION

Carbon steels have to meet some requirement for a wide range of industrial applications. From the results of our previous study as shown in Figure 1, the low carbon steel experienced high oxidation rate.

After exposure at 700°C for 8 cycles, the steel is highly consumed, forming thick iron oxides layer on the steel surface. Cracks mostly appeared in the oxide layer and at the oxide/steel interface. Accordingly, in order to satisfy the requirement for the use of low carbon steel in oxidizing conditions and at high temperatures, the surface treatment is considered to be an effective way to improve its oxidation resistance.

It is well known that the coating deposition have been widely used to reduce the alloy production cost [1], to improve wear, hardness and to act as thermal insulation of bulk materials like oxidation or corrosion resistance applications [2-3]. For the aforesaid purposes, the selecting of an appropriate coating material and composition becomes particularly important because it greatly determines the coating properties and the service life. The FeCrAlY was receiving attractive attention for high temperature oxidation and corrosion resistance applications because of the formation of a protective scale in the external layer [4-5]. In many cases, however, the formation and establishment of a protective oxide layer are more often affected by oxidation conditions as temperature and atmospheres, and also depended on the material composition. Mostly, less protective oxide scales as spinel or metastable  $Al_2O_3$  were formed. The transformation of metastable  $Al_2O_3$  to an  $\alpha$ - $Al_2O_3$  below than 1000°C takes longer time [6]. Another important issue, the cyclic oxidation condition can lead to oxide cracking and/or coating spallation.

In order to fulfill the problems as presented above, the addition of alloying elements can be considered to promote the formation of a protective oxide layer. A number of studies have reported the beneficial effect of some elements as Si and Mo in improving the properties of metals and alloys. Bahaedin Nikrooz, et. al. (2012) reported that the adequate amount of Si addition to stainless steel can promote the formation of  $SiO_2$  layer at the substrate/oxide interface. The formed  $SiO_2$  can also act as the nucleation site for the formation of Cr<sub>2</sub>O<sub>3</sub> scales [7]. Yoshitoshi Saito, et. al. (1998) also pointed out that the crystalline SiO<sub>2</sub> can act as a heterogeneous nucleation site and accelerates the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> transformation [8]. While, the appropriate amount of Mo content has beneficial effects in improving the breakaway oxidation resistance [9]. Evidently, many researchers have also shown an increased interest in attractive silicides material of MoSi<sub>2</sub> for high temperature resistance applications due to its properties such as high melting temperature (2030°C), low density (6.24 g/cm<sup>3</sup>), high hardness (1-1.3 GPa) and excellent oxidation resistance due to the selective oxidation of Si to form a protective SiO<sub>2</sub> scale [10-11].

Based on the points as presented above, this paper attempts to consider the addition of MoSi<sub>2</sub> to improve the FeCrAlTiY oxidation resistance. The primary aim of the present work is to investigate the effect of MoSi<sub>2</sub> addition on the high temperature oxidation behavior of FeCrAlTiY coating deposited on the surface of low carbon steel at 700°C. The coatings were prepared by a flame spraying technique. The oxidation behavior, structure evolutions of the coating before and after high temperature oxidation test were presented and discussed in this paper.

#### 2. EXPERIMENTAL

FeCrAlTiY coatings containing varying amount of  $MoSi_2$  as 0, 10, 20 and 30 % by mass on carbon steel ST41 were prepared by using a flame spray technique. The sample and coating preparation procedures were conducted according to our previous study [12]. Here, we briefly repeated the experimental. For the coating preparation, the commercial plat of low carbon steel was cut into coupons of about 10 mm × 10 mm × 3 mm. Its chemical composition is presented in Table 1.

A hole was made in the top part of the sample to hang the samples during coating process. The substrate surface was ground to abrasive SiC papers (up to #800) and cleaned in an ultrasonic bath using ethanol solution. It was dried and then sand-blasted by using coarse brown fused alumina to enhance the coating and substrate adhesion. Further, the substrate cleaning was carried out using compressed air to eliminate the contaminants.

In the present study, the commercial powders of FeCrAlTiY-Sandvik Materials Technology Ltd. (nominal composition in % mass: balance Fe, 17.2 Cr, 6.6 Al, 0.58 Ti, 0.47 Ni, 0.36 Mn, 0.097 Y, 0.097 Cu) and MoSi<sub>2</sub>-Japan New Metals Co. Ltd. (nominal composition in % mass: balance Mo, 35.8-37.8 Si,  $\leq$  0.05 C,  $\leq$  0.23 Fe,  $\leq$  0.5 O) were selected as powder coating. The XRD patterns and SEM morphologies of the powders are presented in Figures 2 and 3, respectively.

In order to study the effect of MoSi<sub>2</sub> content in the oxidation resistance of FeCrAlTiY coatings, four different coating compositions such as FeCrAlTiY coating with 0, 10, 20 and 30 mass % MoSi<sub>2</sub> were deposited on the surface of ST41 using a flame spray (Metallisation Flamespray MK74). During coating process, the pressure of

oxygen and acetylene was adjusted to 2.07 and 0.83 bars, respectively and the compressed air pressure was set to 1.34 bars. The distance of the sample and spray gun were kept constant carefully of about 20 cm in order to obtain coating thickness uniformity.

The resistance of the coatings toward oxidation at high temperature was evaluated according to the mass gain of oxidized samples. All coated samples were placed in alumina crucible separately. Before it was used, the alumina crucibles were heated at 1000°C for 1h to ensure that the weight of crucible was not changed during the high temperature oxidation test. The samples were then cyclically oxidized in static air of a muffle furnace at 700°C for 8 times. One cycle consists of 20 h exposure at 700°C and 4 h cooled down to room temperature. The mass gain of the samples at each cyclic time was periodically measured using an electronic balance with the accuracy of 0.01 mg.

The phase composition of the coatings was determined by using X-ray diffraction (Rigaku Smartlab). Sample scanning was performed using 40kV and 30mA of Cu-kα radiation and measured at 20-90 deg of diffraction angle, 0.01 deg of stepping width and 0.4 of scanning speed. While, the microstructure evolution and compositional analysis of cross-sectional samples were investigated using scanning electron microscope (SEM Hitachi SU3500) and energy dispersive X-ray spectrometer (EDX Horiba). Observation and EDX analysis were conducted using an accelerating voltage of 20 KV. Based on the results obtained, the effect of MoSi<sub>2</sub> on microstructure and sample oxidation resistance was presented and discussed.

#### 3. RESULTS AND DISCUSSION

#### 3.1 Phase Constituent and Microstructure of FeCrAlTiY-MoSi<sub>2</sub> Coatings

The phase structures formed in the FeCrAlTiY-MoSi<sub>2</sub> coatings deposited on the surface of low carbon steel using a flame spray technique are shown in Figure 4.

According to the result of XRD analysis, three phases formed in the FeCrAlTiY coating without  $MoSi_2$  addition (see Fig. 4(a)) are FeCr,  $Fe(Cr,Al)_2O_4$  and FeO. Meanwhile, another new phases as  $MoSi_2$  and  $Mo_5Si_3$  are found in the FeCrAlTiY coatings with different content of  $MoSi_2$  as 10, 20 and 30 mass%. It is apparent that the intensity of FeCr phase in the FeCrAlTiY coatings has a tendency to decrease with the addition of  $MoSi_2$ . In contrast, the oxides of Fe, Cr and Al are likely to form in the coating. This could be due to that the oxides are covering the metallic compounds. Moreover, the presence of oxides in the coating implies that some coating elements are more favored to oxidize during coating preparation to form FeO and  $Fe(Cr,Al)_2O_4$ . It seems that  $Al_2O_3$  and  $Cr_2O_3$  scales were formed firstly during high temperature coating deposition because of a strong affinity of Al and Cr for the oxygen. The consumed of Al and Cr leads to its coating element depletion. Accordingly, the Fe element was then preferentially oxidized to form FeO. Some amount of FeO were then reacted with  $Al_2O_3$ ,  $Cr_2O_3$  and oxygen, forming  $Fe(Cr,Al)_2O_4$  according to the reaction below.

$$FeO + Al_2O_3 + Cr_2O_3 + \frac{1}{2}O_2 \rightarrow Fe(Cr, Al)_2O_4$$
(1)

It is worth noting that the  $Mo_5Si_3$  phase with intensity different is observed in the FeCrAlTiY-MoSi<sub>2</sub> coatings. Its formation may proceed due to oxidation reaction of  $MoSi_2$  phase through the following reaction,

$$5 \operatorname{MoSi}_{2}(s) + 7 \operatorname{O}_{2}(g) \rightarrow 7 \operatorname{SiO}_{2}(s) + \operatorname{Mo}_{5} \operatorname{Si}_{3}(s)$$
(1)

as reported by previous studies [13-15]. Si from  $MoSi_2$  phase was consumed and reacted with oxygen to form  $SiO_2$  and  $Mo_5Si_3$ . However, as shown in Fig. 4 b, c and d, the  $SiO_2$ peaks reflection is not observed. This may be attributed to that the oxide is in amorphous phase so it is not detected by X-ray diffraction [16].

Figure 5 show the typical SEM cross-sectional microstructures of FeCrAlTiY-MoSi<sub>2</sub> sprayed coatings on low carbon steel using flame spray technique.

The obtained results show a rough coating surface of FeCrAlTiY-MoSi<sub>2</sub>. The thickness of the coating is about 280-350  $\mu$ m. According to the cross-sectional images as shown in Fig. 5, the coating appear to have typical lamellar structures of thermal spray coating containing fully melted particles and partially deformed particles, oxides and pores. From Figs. 5b, c and d, it can also be seen that with the increase of MoSi<sub>2</sub> content, the coatings are susceptible to pores formation. This might be related to the high melting point of MoSi<sub>2</sub> [10-11]. The existence of unmelted or partially melted particles was creating pores within the coating [17-18]. Moreover, from Fig. 5d, the results show that 30 mass% MoSi<sub>2</sub> addition essentially change the coating microstructure. Pores can be seen at the coating/substrate interface. It is generally agree that the coating porosity and adherence will significantly affect the sample oxidation resistance. The presence of pores and cracks can act as a short circuit path for inward oxygen diffusion, resulting in reducing the sample oxidation resistance.

In order to examine the distribution of elements in the FeCrAlTiY-MoSi<sub>2</sub> coatings (white striped area in Fig. 5), we took BSE compositional image and performed EDX elemental maps as presented in Figs. 6. Mostly, the BSE comp image of black, dark and bright areas indicates pore, oxide and metallic phases, respectively. From EDX

elemental maps of FeCrAlTiY coating with different content of MoSi<sub>2</sub>, one of the results show the presence of oxygen distribution in the coating as mark with green color which reveals that some coating elements are already oxidized during coating preparation. This evidence supports the results of XRD analysis as explained above.

In the FeCrAlTiY coating as shown in Fig. 6a, the coating is mostly composed of dark area and bright area. An EDX elemental maps show that the dark area consists of Fe, Cr, Al and O (See Fig. 6a). It seem to be Fe(Cr,Al)<sub>2</sub>O<sub>4</sub> and FeO phases according to the results of X-ray diffraction analysis. The grey area is composed mainly of Fe and Cr with trace amount of Al that should be FeCr phase containing Al. Meanwhile, the microstructure of FeCrAlTiY coatings with 10, 20 and 30 mass% MoSi<sub>2</sub> coatings as shown in Fig. 6b, c and d is almost similar to that of MoSi<sub>2</sub>-free coating that consist mainly of dark area of Fe, Cr, Al and O; and grey area of Fe, Cr and Al. However, bright area of Mo and Si is observed in FeCrAlTiY coatings with varying amount of MoSi<sub>2</sub> that is suspected to be MoSi<sub>2</sub> and Mo<sub>5</sub>Si<sub>3</sub> phases. Mo<sub>5</sub>Si<sub>3</sub> usually form at the SiO<sub>2</sub> and  $MoSi_2$  interface due to Si consumed [14]. However, it is important to note that in the external layer of 30 mass% MoSi<sub>2</sub> coatings, a continuous oxygen distribution can be clearly distinguished. This is one indication that the surface of FeCrAlTiY-30mass% MoSi<sub>2</sub> coating is covered by oxide layer which formed during coating preparation. Even if the formation of oxide during coating preparation prefers to be avoided, its formation may give a potential benefit in providing temporary oxidation protection.

#### 3.2 Oxidation Behavior of FeCrAlTiY-MoSi<sub>2</sub> Coatings.

Figures 7 a and b compare the mass gain per unit areas and the square of mass gain per unit areas of the FeCrAlTiY-MoSi<sub>2</sub> coatings as a function of cyclic oxidation time exposed at  $700^{\circ}$ C for up to 8 cycles in air atmosphere.

The results as shown in Fig. 7a show a clear trend of an increasing the mass gain of FeCrAlTiY-MoSi<sub>2</sub> coatings along the oxidation period. In the initial stage of oxidation, the increase of mass gain is high until the oxide scale was developed on the external layer. Subsequently, the increase of mass gain tends to be slow because the growth of oxide layer is controlled by cations and anions diffusion across the oxide layer. It can be seen in Fig. 7b that the square of mass gain per unit areas of the samples has a tendency to increase linearly with cyclic oxidation time, suggesting that the oxidation of FeCrAlTiY-MoSi<sub>2</sub> coating obeys the parabolic rate law. According to the results as presented in Figs. 7a and b, the oxidation kinetic of FeCrAlTiY coatings was varied depending on MoSi<sub>2</sub> concentration. For 100% FeCrAlTiY coating, the mass gain of the sample is about 0.261 mg/mm<sup>2</sup>. The 10 mass% MoSi<sub>2</sub> addition leads to lowering the mass gain of 100% FeCrAlTiY coating into 0.217 mg/mm<sup>2</sup>. In contrast, the addition of 20 and 30 mass% MoSi<sub>2</sub> appears to enhance the mass gain of 100% FeCrAITiY coating into 0.297 and 0.308 mg/mm<sup>2</sup>, respectively. It is apparent that the mass gain of 30 mass%  $MoSi_2$  addition is smaller compared to the other composition in the first cycle. It then gradually increase for up to eighth cycles, resulting in a larger mass gain than other coatings. This is probably due to the formation of external oxide layer on the FeCrAlTiY-30mass% MoSi<sub>2</sub> coating play a role in providing temporary protection in the initial stage of oxidation. However, after certain time of exposure, the oxide layer

was degraded, promoting accelerated oxidation. As results, the mass gain of 30 mass% MoSi<sub>2</sub> coating is higher than the other samples. The results as presented above suggests that 20 and 30 mass% MoSi<sub>2</sub> additions are considerable worse to the oxidation resistance of 100% FeCrAlTiY coating. Meanwhile, the addition of 10 mass% MoSi<sub>2</sub> has a beneficial effect in improving the oxidation resistance of FeCrAlTiY coating.

## 3.3 Phase Constituent and Microstructure of FeCrAlTiY-MoSi<sub>2</sub> Coatings After Oxidation

Figure 8 shows the XRD patterns of FeCrAlTiY-MoSi<sub>2</sub> coating fabricated by a flame spray technique oxidized at 700°C for 8 cycles.

According to the result of XRD analysis, the main phase was detected in the 100% FeCrAlTiY coating after exposure at 700°C for 8 cycles, namely Fe<sub>2</sub>O<sub>3</sub>. The reflection of coating peaks is not detected in Fig. 8a. This is due to a thickened of oxide layer formed in the external layer of FeCrAlTiY coating after oxidation. As a result, X-ray diffraction could not reach the coating surface. On the other hand, there is no significant different in the coating structure of FeCrAlTiY coating with 10, 20 and 30 mass% MoSi<sub>2</sub> after exposure at 700°C for 8 cycles. The coatings form Fe<sub>2</sub>O<sub>3</sub> and Fe(Cr,Al)<sub>2</sub>O<sub>4</sub> after oxidation at 700°C for 8 cycles. The peak coating reflection as FeCr, MoSi<sub>2</sub> and Mo<sub>5</sub>Si<sub>3</sub> can still be observed as shown in Fig. 8 b, c and d. But it has a tendency to decrease with the increase of MoSi<sub>2</sub> addition in the coatings. The aforementioned results suggest that the oxide scale of FeCrAlTiY coating without MoSi<sub>2</sub> addition is thicker than that of MoSi<sub>2</sub> addition coatings. Moreover, as MoSi<sub>2</sub>

content in the coating increase from 10 to 30 mass%, the thickness of oxide layer is likely to increase.

The microstructure transformation of FeCrAlTiY-MoSi<sub>2</sub> coatings after high temperature oxidation test at  $700^{\circ}$ C for 8 cycles can be observed in Figure 9.

It can be seem in 100% FeCrAlTiY coating, a thick oxide layer with the thickness of about 130  $\mu$ m is formed in the coating surface, resulting a high sample mass gain compared to the 10 mass% MoSi<sub>2</sub> coating. A severe crack formation can also be observed in formed oxide layer and at the oxide/coating interface. In addition, similarly to the other coating composition, pores are still found within the coating layer. With the addition of MoSi<sub>2</sub>, the coatings exhibit less severe oxide crack formation on its surface. The oxide layer of FeCrAlTiY coatings with MoSi<sub>2</sub> (10, 20 and 30 mass%) addition is a thinner compare to that of 100% FeCrAlTiY coating. However, in the 20 and 30 mass% MoSi<sub>2</sub> coating, the oxidation is also favor to occur at the coating/substrate interface. This strongly suggests that the oxygen potential is high at the aforementioned location. This is related to the more porous microstructure of 20 and 30 mass% MoSi<sub>2</sub> coatings before oxidation (see Fig. 5). Accordingly, oxygen is more easily to diffuse inwardly, leading to oxidation at the coating/substrate interface. This is also the reason why the mass gain of 30 and 20 mass% MoSi2 coating is higher than 10 mass% MoSi<sub>2</sub> coating.

Figure 10 shows the cross-sectional BSE SEM images and corresponding EDX elemental maps of FeCrAlTiY-MoSi<sub>2</sub> coatings after oxidation at 700°C for 8 cycles. It can be seem from the result of EDX element maps of Fig. 10a that the external layer of FeCrAlTiY coating after high temperature oxidation test consists mainly of Fe and O

with a minor amount of Cr and Al. While beneath the aforesaid layer, the oxide is composed of Fe, Cr, Al and O. In accordance to the result of XRD analysis in Fig. 8a, the external oxide layer corresponds to  $Fe_2O_3$ , mainly. Underneath  $Fe_2O_3$ , the oxide layer is probably composed mostly of Fe(Cr,Al)<sub>2</sub>O<sub>4</sub> as detected in the coating before oxidation. For the FeCrAlTiY coatings with MoSi<sub>2</sub> addition, the result of EDX elemental maps shows that thin external oxide layer is rich in Fe and O which is estimated as Fe<sub>2</sub>O<sub>3</sub>. While beneath the Fe<sub>2</sub>O<sub>3</sub>, the oxide layer consists of Fe, Cr, Al and O that should be  $Fe(Cr,Al)_2O_4$ . Evidently from Fig. 10, the  $Fe_2O_3$  external layer formed in the FeCrAlTiY coating is thicker compared to that of FeCrAlTiY coatings with the addition of MoSi<sub>2</sub>. This suggests that the Fe outward diffusion thought spinel oxide is decreased with the addition of MoSi<sub>2</sub> to the coating. In addition, the results of EDX elemental maps also show that the formed oxide layer at the coating substrate interface of 20 and 30 mass% MoSi<sub>2</sub> coating contain mainly of Fe and O that is suspected to be due to oxidation of carbon steel substrate as effect of oxygen inward diffusion through coating pores. The obtained results as presented above suggest that the FeCrAlTiY-10 mass% MoSi<sub>2</sub> coating exhibit best oxidation resistance after exposure at 700°C for 8 cycles.

#### 4. CONCLUSIONS

This paper describes the results of FeCrAlTiY-MoSi<sub>2</sub> coatings prepared on low carbon steel using a flame spray technique. The effects of MoSi<sub>2</sub> addition on the resistance of FeCrAlTiY coatings toward high temperature oxidation at 700°C were studied for up to 8 cycles. The results obtained can be summarized as follows:

- 1. A flame spray technique allows to produce the FeCrAlTiY coatings with different content of MoSi<sub>2</sub> on the surface of low carbon steel.
- The MoSi<sub>2</sub> content affects the coating microstructure of FeCrAlTiY coatings. Pores, oxides, fully and partially melted particles are found in the FeCrAlTiY-MoSi<sub>2</sub> coatings. The coating becomes more porous with the increase of MoSi<sub>2</sub> content.
- FeCrAlTiY coating forms a thick Fe<sub>2</sub>O<sub>3</sub> scale after exposure for 8 cycles at 700°C. Cracks are also mostly found in the oxide layer and at the oxide/coating interface.
- 4. For oxidation resistance application, the addition of 10 mass% MoSi<sub>2</sub> strengthens the FeCrAlTiY coating oxidation resistance. It exhibits effective protection for carbon steel against high temperature oxidation among the other composition.
- 5. On the contrary, the addition of 20 and 30 mass% MoSi<sub>2</sub> are lowering the FeCrAlTiY coating oxidation resistance. The oxygen diffusions through pores in the coating affect the oxidation at the coating substrate interface, resulting in oxides formation.

#### ACKNOWLEDGEMENTS

The authors thank Mr. Ciswandi and Mr. Edi Setiawan for technical support and discussion. The authors also acknowledge Research Center for Physics-Indonesian Institute of Sciences for providing characterization facilities. This work is financially supported by Program Unggulan 2018 of Indonesian Institute of Sciences.

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S	Cu	Ti	Р	Ni	Cr	Al	Та	С	Si	Mn	Fe
0.0029	0.0108	0.0133	0.0174	0.0199	0.0419	0.0435	0.053	0.0989	0.239	0.499	98.90

Table 1 Chemical composition of low carbon steel



Figure 1 Cross-sectional BSE SEM image and EDX elemental map analysis of low carbon steel after oxidation at 700°C for 8 cycles in air.



Figure 2 XRD patterns of (a)  $MoSi_2$  and (b) FeCrAlTiY powders



Figure 3 SE SEM images of (a)  $MoSi_2$  and (b) FeCrAlTiY powders



Figure 4 XRD patterns of FeCrAlTiY coatings with (a) 0, (b) 10, (c) 20 and (d) 30 mass%  $MoSi_2$ 



Figure 5 Cross-sectional SE SEM images of FeCrAlTiY coatings with (a) 0, (b) 10, (c) 20 and (d) 30 mass% MoSi<sub>2</sub>



Figure 6 The cross-sectional BSE SEM images and corresponding EDX elemental maps of FeCrAlTiY coatings with (a) 0 and (b) 10

mass% MoSi<sub>2</sub>



Figure 6 The cross-sectional BSE SEM images and corresponding EDX elemental maps of FeCrAlTiY coatings with (c) 20 and (d)

30 mass% MoSi<sub>2</sub>



Figure 7 The mass gain per unit areas and square of mass gain per unit areas of FeCrAlTiY MoSi<sub>2</sub> coatings after exposure at 700°C for 8 cycles in air



Figure 8 XRD patterns of FeCrAlTiY coatings with (a) 0, (b) 10, (c) 20 and (d) 30 mass% MoSi<sub>2</sub> after exposure at 700°C for 8 cycles in air



Figure 9 Cross-sectional SEM images of FeCrAlTiY coatings with (a) 0, (b) 10, (c) 20 and (d) 30 mass%  $MoSi_2$ 



Figure 10 EDX elemental maps of FeCrAlTiY coatings with (a) 0 and (b) 10 mass% MoSi<sub>2</sub> after exposure at 700°C for 8 cycles in air



Figure 10 EDX elemental maps of FeCrAlTiY coatings with (c) 20 and (d) 30 mass% MoSi<sub>2</sub> after exposure at 700°C for 8 cycles in

air

### **Table Captions**

Table 1 Chemical composition of low carbon steel

#### **Figure Captions**

Figure 1 Cross-sectional BSE SEM image and EDX elemental map analysis of low carbon steel after oxidation at 700°C for 8 cycles in air.

Figure 2 XRD patterns of (a) MoSi<sub>2</sub> and (b) FeCrAlTiY powders

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Figure 4 XRD patterns of FeCrAlTiY coatings with (a) 0, (b) 10, (c) 20 and (d) 30 mass% MoSi<sub>2</sub>

Figure 5 Cross-sectional SE SEM images of FeCrAlTiY coatings with (a) 0, (b) 10, (c) 20 and (d) 30 mass% MoSi<sub>2</sub>

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Figure 6 The cross-sectional BSE SEM images and corresponding EDX elemental maps of FeCrAlTiY coatings with (c) 20 and (d) 30 mass% MoSi<sub>2</sub>

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Figure 9 Cross-sectional SEM images of FeCrAlTiY coatings with (a) 0, (b) 10, (c) 20 and (d) 30 mass% MoSi<sub>2</sub>

Figure 10 EDX elemental maps of FeCrAlTiY coatings with (a) 0 and (b) 10 mass%  $MoSi_2$  after exposure at 700°C for 8 cycles in air

Figure 10 EDX elemental maps of FeCrAlTiY coatings with (c) 20 and (d) 30 mass% MoSi<sub>2</sub> after exposure at 700°C for 8 cycles in air

## Improvement of Carbon Steel Resistance Against High Temperature Oxidation and Corrosion by Flame Sprayed FeCrAlTiY-30 mass% CoNiCrAlY Coating Using N<sub>2</sub> Pressure

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Abstract. Flame spray technique with nitrogen pressure was used to deposit FeCrAlTiY-30 mass% CoNiCrAlY coating on the surface of low carbon steel. The resistance of the sample against oxidation and corrosion at high temperature was studied cyclically at 700°C for 8 times. The sample was rapidly heated in a furnace at 700°C for 20 hours and then cooled for 4 hours at room temperature. XRD and SEM-EDX were used to investigate the phase composition and morphologies of the coating before and after high temperature oxidation and corrosion test. For corrosion evaluation, the test samples was sprayed using 20 mass% NaCl solution. After the test, it was found that the flame sprayed FeCrAlTiY-30 mass% CoNiCrAlY coating with N<sub>2</sub> pressure effectively enhances the resistance of carbon steel toward oxidation and corrosion at high temperature due to the formation of FeCr, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, (Ni,Co)Cr<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe(Cr,Al)<sub>2</sub>O<sub>4</sub>, respectively. On the contrary, the coating was degraded more easily in 20 mass% NaCl containing atmosphere than in air atmosphere, suggesting that the corrosion attack is more severe than oxidation.

#### **INTRODUCTION**

Carbon steels have been widely used for structural applications of industrial production because of its relativity low cost and good mechanical properties. But it has low resistance to oxidation and corrosion [1-5]. Piping systems in geothermal gas originating from production wells must receive a special attention in terms of oxidation and corrosion resistance and the strength of the material used during applications at high temperatures in the environments containing corrosive gases. The presence of corrosive gases in air (such as chlorine and sulfur) can accelerate the corrosion attack of carbon steels and alloys. The gas phase corrosion is very influential against high temperature corrosion [6].

Previously, [7] we have studied several compositions of FeCrAlTiY coatings with 0, 10, 20 and 30 mass% MCrAlY (M = Co and Ni) content on carbon steel by a flame spray technique. The coating deposition was carried

out using compressed air as a carrier gas. From the results of the study, we obtained that the FeCrAlTiY-30 mass% CoNiCrAlY coating plays a role in enhancing the resistance of carbon steel to oxidation at high temperature. However, during the spraying process, some coating elements are likely to oxidize that may occur due to exposure of air atmosphere and compressed air of gas carrier. This phenomenon is believed affecting the coating oxidation resistance because the coating becomes depleted with elements which forms a protective oxide layer. Therefore, it is necessary to consider the changing of carrier gas from compressed air to inert gas for reducing the coating elements oxidation during sample preparation. In the present study, we described the optimalization results of FeCrAlTiY-30 mass% CoNiCrAlY coating preparation using nitrogen as carrier gas. In addition, we presented the results of its oxidation and corrosion resistance toward air and atmosphere containing 20 mass% NaCl at 700°C.

#### **EXPERIMENTAL PROCEDURES**

The carbon steel ST 41 with a size of 10 mm  $\times$  10 mm  $\times$  3 mm was used as substrate and its composition was shown in Table 1.

		]	TABLE 1.	Chemical	compositio	on of carbo	n steel ST	[ 41 (in ma	.ss%)		
Fe	Mn	Si	С	Cr	Cu	Ni	Та	Р	S	Ti	Al
98.90	0.499	0.239	0.0989	0.0419	0.0108	0.0199	0.053	0.0174	0.0029	0.0133	0.0435

Carbon steel was polished using abrasive SiC papers for removing the contaminants on the surface of the substrate. Polished samples were then sterilized in ethanol solution with ultrasonic cleaner. The sand blasting process was carried out with a pressure of 12 bars to enhance the bonding between coating and substrate.

Two types of coating powders were used in our study, namely FeCrAlTiY from Sandvik Materials Technology Ltd. dan CoNiCrAlY from Sulzer Metco Co. Ltd. The powder coating composition used is FeCrAlTiY-30 mass% MCrAlY. The aforesaid powder composition was mixed for 30 minutes using a rotary milling. It was then putted into a flame spraying (Metallisation Flamespray MK74) powder feeder. The combustion of acetylene and oxygen gases was used to heat the powder materials and impacted on the steel surface with nitrogen pressure as carrier gas.

The oxidation resistance of coated sample was examined in a box muffle furnace at 700°C for 20 hours and cooled for 4 hours to examine the mass change, repeating for up to 8 times. While for high temperature corrosion test, the NaCl deposit was prepared by spraying 20 mass% NaCl solution onto the surface of the sample. The temperature and cyclic time for corrosion test were similar to the oxidation test. The kinetic of oxidation and corrosion was evaluated by measuring the mass changes per surface area of the samples as function of cyclic times

The phase constituent of the sample (as coating and after oxidation-corrosion test) was determined using X-ray diffraction. Microstructure and elemental analysis of the sample were evaluated by scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDX), respectively.

#### **RESULTS AND DISCUSSION**

#### **Coating Characteristics Before High Temperature Oxidation And Corrosion Test**

Figures 1 shows the X-ray diffraction pattern of FeCrAlTiY-30 mass% CoNiCrAlY coating prepared by flame spray technique using N<sub>2</sub> pressure. Substrate coated with FeCrAlTiY-30 mass% CoNiCrAlY has 4 phases namely FeCr, (Ni,Co)Cr<sub>2</sub>O<sub>4</sub>, Fe(Cr,Al)<sub>2</sub>O<sub>4</sub> and FeO. The presence of oxides phase informs that a number of coating elements have been oxidized when the coating process takes place. Even if the XRD pattern shows that the FeCr peaks are sharply observed. The oxide formation indicates that the use of nitrogen gas as a carrier gas is not enough to eliminate the oxidation of coating elements. There is still contribution of oxygen used for combustion or oxygen from the environment in the oxides formation [8]. For the spinel formation, it can be explained briefly as follow. The high affinity of Al and Cr for oxygen resulted in the formation of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> which then reacted with FeO to form FeAl<sub>2</sub>O<sub>4</sub> dan FeCr<sub>2</sub>O<sub>4</sub>. On the contrary, the spinel (Ni,Co)Cr<sub>2</sub>O<sub>4</sub> formation occurs because of the reaction between NiO and Cr<sub>2</sub>O<sub>3</sub>; and CoO with Cr<sub>2</sub>O<sub>3</sub> to form NiCr<sub>2</sub>O<sub>4</sub> and CoCr<sub>2</sub>O<sub>4</sub>. The formed spinel effectively provides protection against oxidation and corrosion [9-10].



FIGURE 1. XRD pattern of FeCrAlTiY-30 mass% CoNiCrAlY coating

Figure 2 shows the cross-sectional microstructures of FeCrAlTiY coating with 30 mass% CoNiCrAlY prepared using  $N_2$  pressure. The cross-sectional images of the samples confirm that the coating powder was successfully deposited on the substrate surface with a thickness of around  $\pm$  337 µm.



FIGURE 2. (a) BSE SEM cross-sectional microstructure and (b) corresponding EDX spectrum analysis of FeCrAITiY coating with 30 mass% CoNiCrAIY

Flamonto	Element Composition (at%)								
Elements	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4	Spectrum 5				
0	69.68	59.06	7.20	85.04	71.57				
Al	15.78	6.62	0.14	3.38	16.42				
Ti	0.02	0.33	0.01	0.08	0.53				
Cr	5.93	6.03	2.45	3.05	2.78				
Fe	0.35	27.34	88.35	4.28	2.45				
Со	5.07	0.44	1.23	2.07	3.51				
Ni	3.01	0.17	0.62	2.10	2.67				
Y	0.16	-	-		0.08				

TABLE 2. The results of SEM-EDX point analysis of FeCrAlTiY-30 mass% CoNiCrAlY

Visually, there are 4 types of contrast different in the coating results (see Fig. 2a), that is light, gray, dark and black areas. The light part is a very dominant compared to dark areas. The results of EDX point analysis in the corresponding area of FeCrAlTiY-30 mass% CoNiCrAlY (Fig. 2b) coating are presented in Table 2. The dark area (see Spectrum 1) consists of 69.68 at% O, 15.78 at% Al, 5.93 at% Cr, 5.07 at% Co, and 3.01 at% Ni with minor elements of Fe, Ti, Y that is suspected to be Al-oxides and (Ni,Co)Cr<sub>2</sub>O<sub>4</sub> phases. The other dark area (see Spectrum

2) consists of 59.06 at% O, 27.34 at% Fe, 6.03 at% Cr and 6.62 at% Al with small content of Co, Ni, Ti which is suspected to be  $Fe(Cr,Al)_2O_4$  and FeO phases as detected by X-ray diffraction. The bright area (see Spectrum 3) consists of 88.35 at% Fe, 2.45 at% Cr and 7.20 at% O with minor elements of Al, Ti, Co, Ni which should be FeCr phase as detected by X-ray diffraction. The black area (see Spectrum 4) consists mainly of 85.04 at% O that should be pore. The dark area (see Spectrum 5) consists of 71.57 at% O, 16.42 at% Al, 3.51 at% Co, 2.78 at% Cr, 2.67 at% Ni, 3.51 at% Co, and 2.45 at% Fe with small content of Ti, Y that is probably Al oxides,  $Fe(Cr,Al)_2O_4$  and (Ni,Co)Cr<sub>2</sub>O<sub>4</sub> phases. The Al-oxides is not detected by X-ray diffraction due to that its fraction is relatively small compared to the other phases. The cross-sectional microstructures of coating contain a number of pores. Previous study reported that the use of flame spray technique produces a number of pores compared with other thermal spray techniques [11].

#### Coating Characteristic After Exposure At 700°C For 8 Cycles

#### **Kinetic Oxidation And Corrosion Test**

Figure 3 shows the mass gain curve of FeCrAlTiY-30 mass% CoNiCrAlY coating after exposure at 700°C for 8 cycles as a function of cyclic oxidation and corrosion times. The mass gain of the sample increases with the increase of exposure time.



FIGURE 3. Mass gain curves of FeCrAlTiY-30 mass% CoNiCrAlY coatings after oxidation and corrosion at 700°C for 8 cycles (Catatan Gambar unit Mass Gain mg/mm<sup>2</sup>  $\rightarrow$  mg/mm<sup>2</sup>, dan angka 0 pada sumbu x overlapping)

Based on Fig. 3 the oxidized samples had lower mass gain than corroded sample. It is about 0.2017 mg/mm<sup>2</sup> and 0.6026 mg/mm<sup>2</sup>, respectively. According to our previous research [7] the mass gain of sample prepared using a flame spray technique with compressed air as carrier gas was about 0.247 mg/mm<sup>2</sup>. This value is higher compared to that of nitrogen carrying gas, as aforementioned. This suggests that the use of nitrogen as a carrier gas to replace the compressed air during coating preparation is better than compressed air. Although, it is still not enough to prevent oxidation of coating elements.

The results of this study also show that though the corrosion test temperature of this study is lower than a melting temperature of NaCl (801°C) [12], it proves that the existence of NaCl deposits on the coating surface can accelerate the corrosion process. As shown in Fig. 3, the corrosion characteristics during the first cycle, mass gain of the sample increases rapidly. However, after the first cycle the mass gain almost linearly increased until the 8<sup>th</sup> cycles reached 0.6026 mg/mm<sup>2</sup>. In this study, we also performed the corrosion test for the uncoated sample. The mass gain of low carbon steel after 8 cycles exposure is about 0.8073 mg/mm<sup>2</sup>. The obtained results suggest that the FeCrAITiY-30 mass% CoNiCrAIY coating is effective to improve the oxidation and corrosion resistance of low carbon steel.

#### **Coating Characteristics After High Temperature Oxidation And Corrosion Test**

Figures 4 (a) and (b) show the results of XRD analysis of FeCrAlTiY-30 mass% CoNiCrAlY coating after oxidation and corrosion test at 700°C for 8 cycles. The peaks reflection of substrate coated with FeCrAlTiY-30 mass% CoNiCrAlY after oxidation test (Fig. 4(a)) corresponds to 4 phases namely FeCr,  $(Ni,Co)Cr_2O_4$ ,  $Al_2O_3$  and Fe<sub>2</sub>O<sub>3</sub>. While Fig. 4(b) after corrosion test, it consists of 3 phases namely  $Al_2O_3$ ,  $Fe_2O_3$ , and  $Fe(Cr,Al)_2O_4$ .



FIGURE 4. XRD patterns of FeCrAlTiY-30 mass% CoNiCrAlY coating after (a) oxidation and (b) corrosion test at 700°C for 8 cycles



FIGURE 5. (a) BSE SEM cross-sectional microstructures and (b) EDX analysis in the FeCrAlTiY-30 mass% CoNiCrAlY coating after oxidation test in air at 700°C for 8 cycles

	air at 700°C for 8 cycles									
Element	Element Composition (at%)									
Element	Spectrum 1	Spectrum 2	Spectrum3							
0	3.45	44.28	3.40							
Al	0.29	14.74	7.71							
Cr	0.34	19.03	16.34							
Fe	63.61	1.80	70.98							
Со	31.43	14.81	0.70							
Ni	0.88	5.04	0.45							

**TABLE 3**. The results of EDX point analysis after oxidation test in air at 700°C for 8 cycles

Figures 5 and 6 show the results of characterization using SEM and EDX point analysis in the corresponding area of FeCrAlTiY-30 mass% CoNiCrAlY coating after oxidation and corrosion test at 700°C for 8 cycles, respectively. It can be seen from Fig. 5(a) that after oxidation test in air at 700°C for 8 cycles, the coating and oxide

layers have a thickness of around  $\pm$  346 µm. The results of EDX point analysis in the specific area in Fig. 5b are presented in Table 3. The grey area (see Spectrum 1) is composed by 3.45 at% O, 63.61 at% Fe, and 31.43 at% Co with a minor Al, Cr and Ni. The Spectrum 2 consists of 44.28 at% O, 14.74 at% Al, 19.03 at% Cr,14.81 at% Co, 5.04 at% Ni and 1.80 at% Fe which should be (Ni,Co)Cr<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> phases. The Spectrum 3 consists of 3.40 at% O, 70.98 at% Fe, 7.71 at% Al, and 16.34 at% Cr which is suspected to be FeCr, mainly. Here, the Fe-oxide was not detected by EDX analysis, probably due to randomly distributed on the coating surface.



FIGURE 6. (a) BSE SEM cross-sectional microstructures and (b) EDX analysis in the FeCrAlTiY-30 mass% CoNiCrAlY coating after corrosion test at 700°C for 8 cycles

TABLE 4. The results of EDX point analysis after corrosion test in the atmosphere containing 20
mass% NaCl at 700°C for 8 cycles

Element	Element Composition (at%)								
Element	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum4	Spectrum5				
0	65.90	32.53	72.52	43.70	67.92				
Na	0.18	1.66	0.41	1.88	0.47				
Al	21.50	9.80	1.69	19.75	5.34				
Cl	0.14	0.21	-	0.17	0.28				
Cr	11.15	7.23	0.11	1.52	6.44				
Fe	0.40	41.21	20.89	26.01	14.63				
Со	0.52	5.79	4.30	3.93	3.69				
Ni	0.14	1.58	0.08	3.03	0.93				

Figure 6(a) shows the results of BSE SEM cross-sectional microstructures of FeCrAlTiY-30 mass% CoNiCrAlY coating after corrosion test. The coating and oxide scales have a thickness of around  $\pm$  673 µm. It is much thicker compared to that of oxidized sample. According to the results of EDX analysis as presented in Table 4, the Spectrum 1 consists of 65.90 at% O, 21.50 at% Al and 11.15 % at Cr and very small Na, Cl, Fe, Co, Ni which is probably composed mainly of Al<sub>2</sub>O<sub>3</sub> phase. The Spectrum 2 consists of 32.53 at% O, 41.21 at% Fe, 7.23 at% Cr and 9.80 at% Al which is suspected to be Fe<sub>2</sub>O<sub>3</sub> and Fe(Cr,Al)<sub>2</sub>O<sub>4</sub>. The dark area (see Spectrum 3) consists of 72.52 at% O and 20.89 at% Fe that is suspected to be Fe<sub>2</sub>O<sub>3</sub> phase as detected by X-ray diffraction. The grey area (see Spectrum 5) consists of 67.92 at% O, 14.63 at% Fe, 6.44 at% Cr, and 5.34 at% Al which is suspected to be Fe(Cr,Al)<sub>2</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> phases as detected by X-ray diffraction. The black area (see Spectrum 4) consists mainly of 43.70 at% O, 26.01 at% Fe and 19.75 at% Al. Evidently, the NaCl deposits on the surface of the sample can accelerate the corrosion process (see Fig. 6). This is probably due to the reaction between metallic elements and NaCl may form volatile species that is creating defects in the coating [13]. The results of this study show that after exposure for 8 cycles, thick oxide layer forms on the external layer and at the coating/substrate interface. The formation of oxides at the coating/substrate interface indicates that the oxygen was diffused inwardly through defects in the coating and substrate elements oxidation.

#### CONCLUSIONS

The FeCrAlTiY-30 mass% CoNiCrAlY coating with  $N_2$  pressure enhances the resistance of low carbon steel toward oxidation and corrosion at high temperature. After high temperature oxidation and corrosion test, the coating forms oxide scales consisting of Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, (Ni,Co)Cr<sub>2</sub>O<sub>4</sub>, and Fe(Cr,Al)<sub>2</sub>O<sub>4</sub>, depending on atmospheric condition (air or air containing NaCl). In addition, the results reveal that the presence of NaCl in air accelerates the degradation of coating and substrate.

#### ACKNOWLEDGMENT

This work was partially supported by Indonesian Institute of Sciences. Characterization facilities provided by Research Center for Physics, Indonesian Institute of Sciences were gratefully acknowledgements.

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## High Temperature Oxidation Resistance of FeCrAITiY-MCrAIY (M = Co and Ni) Coatings on Carbon Steel Prepared by Flame Spray Technique

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Received February 12, 2019; revised May 10, 2019; accepted May 16, 2019

Abstract—Four different composition of FeCrAlTiY-x MCrAlY (M = Co and Ni, x = 0, 10, 20, and 30 in mass %) coatings were prepared onto carbon steel substrate using a flame spray technique. The high temperature oxidation resistance of the coating and uncoated samples was studied cyclically at 700°C for 8 times. X-ray diffraction (XRD) and scanning electron microscope equipped with energy dispersive X-ray spectrometer (SEM-EDX) were used to investigate the phase composition and morphologies of the coating before and after oxidation. Depending on the coating composition, the coatings are composed of FeCr, Fe(Cr,Al)<sub>2</sub>O<sub>4</sub>, (Co,Ni)Cr<sub>2</sub>O<sub>4</sub> and FeO. After high temperature oxidation test, it was found that the carbon steel experienced high oxidation rate at the aforesaid temperature, forming a thick Fe-oxides layer. Even if a protective Al<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub> layer is not formed on the coating surface, the flame sprayed FeCrAlTiY–MCrAlY coatings effectively improve the resistance of carbon steel toward oxidation at high temperature due to the formation of Fe<sub>2</sub>O<sub>3</sub> and spinel oxides. According to the results, the 30 mass % MCrAlY coating exhibited a lowest mass gain after exposure at 700°C for 8 cycles.

*Keywords:* FeCrAlTiY, MCrAlY, carbon steel, coating, flame spray, oxidation **DOI:** 10.1134/S2070205120010219

#### 1. INTRODUCTION

The mechanical strength and resistance of material toward oxidation and corrosion are important factors in selecting materials for high temperature applications. Carbon steels have been widely used for structural aplications because of its lower cost and good mechanical properties. The critical issues for the use of low carbon steel with the increase of operating temperature are oxidation and corrosion resistance. The potential application of this material is restricted when it is exposed to high temperature and oxidizing atmospheres [1-3]. This leads to the thickness loss of the sample due to iron oxidation, forming a thick Feoxides layers consisting of Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and FeO on the steel surface [3-6]. The steels tend to easily oxidize at higher temperatures. Accordingly, surface treatment is required to overcome the aforesaid limitations.

FeCrAlY [7, 8] and MCrAlY (M = Co and/or Ni) [9, 10] either as alloys and coatings have been intensively studied due to their resistance toward oxidant and chemical attack at high temperature and aggressive environments. However, the development of materials for advanced energy applications still encounters some challenges because their structural and high temperature properties such as the formation of a protective oxide layer are often affected by its composition and oxidizing conditions including temperature, time and atmosphere. Modifying the material composition can be considered to enhance its oxidation resistance. Accordingly, it is important to investigate and clarify whether the combination of both materials, FeCrAITiY and MCrAIY, applied as composite coating can possibly improve the oxidation resistance of the carbon steel at high temperature.

Many studies utilized thermal spray coating techniques such as high velocity oxygen fuel (HVOF) [9, 11, 12], atmospheric plasma spray coating (APS) [13] and flame spray techniques [14–19] to prepare the metallic or nonmetallic coatings for oxidation, corrosion, and wear resistant coating applications. Basically, the feedstocks of powder, rod or wire are heated 1 into a molten or semimolten state and then accelerated toward a substrate surface to form a coating layer [14,



**Fig. 1.** BSE SEM images of (a) FeCrAITiY dan (b) MCrAIY powders.

20]. It is noteworthy that the coating preparation using a flame spray method has several advantages, such as easy to use, low cost, lower flame temperatures (prevent thermal decomposition) [19], quiet operation and applicable to spray various materials. A number of studies used this technique to deposit Fluorhydroxyapatite [19], FeCr [14, 15], composite [16], porous hydroxyapatite coatings [17] and  $Y_2O_3$  film [18] on the various substrate materials.

In this study we reported the high temperature oxidation characteristics of FeCrAlTiY coatings containing 0, 10, 20, and 30 mass % MCrAlY. It was expected that the addition of MCrAlY could promote the formation of a protective oxide scale and enhance the resistance of sample against oxidation. The coating were deposited on the surface of low carbon steel using a flame spray technique. Their resistance against oxidation at high temperature was studied at 700°C for 8 cycles and compared to the low carbon steel. X-ray diffraction and SEM-EDX were used to study the phase and microstructure of the coating before and after oxidation.

#### 2. EXPERIMENTAL

#### 2.1 Sample Preparation

In this study, carbon steel namely ST 41 (98.90 Fe, 0.499 Mn, 0.239 Si, 0.0989 C, 0.0419 Cr, 0.0108 Cu, 0.0199 Ni, 0.053 Ta, 0.0174 P, 0.0029 S, 0.0133 Ti, and 0.0435 Al in wt %) with a size of  $1 \times 1 \times 0.3$  cm was used as substrate. A small hole with 1 mm in diameter was drilled in the top-middle of the substrate. It was used to hang the sample during coating process. For coating preparation, the surface of the samples was mechanically polished using various grit of abrasive SiC papers ranging in size from #150 to #800 to obtain a flat surface and to remove the scales and contaminants. The samples were then ultrasonically cleaned in ethanol solution for 10 minutes and dried using hot blowing air. Subsequently, the sample surface was

Table 1. Nominal composition of FeCrAlTiY powder

Element	Cr	Al	Ti	Ni	Mn	Y	Cu	Fe
mass %	17.2	6.6	0.58	0.47	0.36	0.097	0.097	Balance



**Fig. 2.** X-ray diffraction patterns of (a) FeCrAlTiY dan (b) MCrAlY powders.

sand blasted using brown fused alumina with a pressure of 12 bar in order to increase the bond strength between coating and substrate. Careful substrate cleaning after sand blasting was carried out to remove the contaminants from the substrate surface.

#### 2.2 Coating Powder and Composition

Two kinds of commercial powders as FeCrAlTiY (Sandvik Materials Technology Ltd) and MCrAlY with M = Co and Ni (Sulzer Metco Co. Ltd) with an average particle size of about 106 and 45 µm, respectively were used as starting material in this study. Both powders have a spherical shape as shown in the BSE SEM images of Fig. 1 and should be able to pass through the flame spray nozzle. The MCrAlY powder might play a role to fill the gaps or pores between the powder of FeCrAlTiY. The nominal composition of FeCrAlTiY and MCrAlY powders is given in Tables 1 and 2, respectively with the powder diffraction patterns presented in Fig. 2.

Four compositions of coating powders as FeCrAl-TiY - 0, 10, 20 and 30 mass % MCrAlY were prepared. In order to obtain a homogeneous powder mixture, each composition was mixed for 30 minutes using a rotary milling. The powder was loaded into powder feeder of a flame spraying (Metallisation Flamespray MK74). In this system, acetylene and oxygen gases were used as energy source to produce a flame for heating the feedstock materials and to impact the molten or semimolten particles on the steel surface. The

compressed air played a role for powder particle carrier/acceleration and spray gun cooling. Moreover, it was used to turn a vibrator assembly to overcome the difficulty of feeding powder. The flame spraying process was performed manually with deposition parameters are presented in Table 3.

#### 2.3 High Temperature Oxidation Test

Before high temperature oxidation test, the samples were put in alumina crucible, weighted using an electronic balance and oxidized in ambient air at 700°C for 8 cycles. The sample was rapidly heated in a muffle furnace at 700°C for 20 hours and then cooled for 4 hours at room temperature. The aforesaid heating and cooling, namely cyclic oxidation test were repeated for up to 8 times. The mass gain was regularly measured during sample cooling. The oxidation kinetic of sample was evaluated from the difference in mass of the sample after and before oxidation test which is then divided by initial surface area of the sample. The results were plotted in the curve of high temperature oxidation kinetic. In this study, the oxidation resistance of the coatings was compared to the uncoated low carbon steel.

#### 2.4 Characterizations

X-Ray Diffraction (XRD) analysis with Cu-Kga radiation ( $\lambda = 1.541$  Å) was used to determine the phase constituent of the coating before and after high temperature cyclic oxidation test. The XRD measurement was conducted using Rigaku Smartlab X-ray diffractometer (40 kV, 30 mA) with the scanning range of 20 from 20–90 deg, scanning speed of 0.4 and stepping width of 0.01 deg. For the cross-sectional coating analysis, the samples were resin mounted, cross-sectionally cut using abrasive cutting machine, polished using various grit of SiC papers for up to mirror finished and cleaned with flowing water. The composition of the coating was then examined by mean of Hitachi SU3500 Scanning Electron Microscope (SEM) at accelerating voltage of 20 kV equipped with an Energy Dispersive X-Ray Spectrometer (EDX).

#### 3. RESULTS AND DISCUSSION

#### 3.1 Coating Characteristics

**3.1.1. Phase Structure.** Figure 3 show the X-ray diffraction patterns of low carbon steel and FeCrAlTiY coatings containing 0, 10, 20 and 30 mass % MCrAlY, respectively prepared by a flame spray technique.

For the comparison, the XRD pattern of the substrate without coating is presented in Fig. 3a. It can be seen that the sharp and narrow peaks of carbon steel substrate consists of three peaks, corresponding to Fe phase. The effect of coating composition on the phase formation of FeCrAITiY–MCrAIY coatings prepared by a flame spray technique can be explained as follow.

 Table 2. Nominal composition of MCrAlY (M=Co and Ni) powder

Element	Co	Ni	Cr	Al	Y
mass %	38.5	32	21	8	0.5

 Table 3.
 Flame spray parameters

0.83 bar
2.07 bar
1.34 bar
20 cm

For the FeCrAlTiY coating, three phases consisting of FeCr metallic phase and Fe(Cr,Al)<sub>2</sub>O<sub>4</sub>, FeO oxides phases are detected by XRD analysis. Initially, Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> seem to be formed due to Al and Cr affinity for the oxygen. However, they are subsequently solid state reacted with FeO to form FeAl<sub>2</sub>O<sub>4</sub> [21, 22] and FeCr<sub>2</sub>O<sub>4</sub> [23, 24]. In this study, it was indicated by the formation of Fe(Cr,Al)<sub>2</sub>O<sub>4</sub> as detected by XRD analysis. The phase formed in the FeCrAlTiY coatings containing various amount of MCrAlY is almost similar to that of FeCrAlTiY coating without MCrAlY addition. However, the (Ni,Co)Cr<sub>2</sub>O<sub>4</sub> phase is also identified in the FeCrAlTiY coatings with 10, 20 and 30 mass %



**Fig. 3.** X-ray diffraction patterns of (a) low carbon steel, FeCrAlTiY coatings with (b) 0, (c) 10, (d) 20 and (e) 30 mass % MCrAlY.



**Fig. 4.** BSE-SEM cross-sectional microstructures of FeCrAlTiY coatings with (a) 0, (b) 10, (c) 20 and (d) 30 mass % MCrAlY.

MCrAlY. Similarly to  $Fe(Cr,Al)_2O_4$ , the (Ni,Co)Cr<sub>2</sub>O<sub>4</sub> spinel structure is formed due to solid state reaction of NiO with Cr<sub>2</sub>O<sub>3</sub> and CoO with Cr<sub>2</sub>O<sub>3</sub>, forming NiCr<sub>2</sub>O<sub>4</sub> and CoCr<sub>2</sub>O<sub>4</sub>, respectively. Tiantian Zhang et al. (2016) also reported that the spinels can provide the protection against oxidation and corrosion [13].

No phase different is found in the MCrAlY-added coatings. From the results as shown in Fig. 3, the diffraction peak of FeCr phase is likely to decrease and the oxides peaks appears to increase with the addition of MCrAlY. The presence of oxides peaks in all coated samples before high temperature oxidation test indicates that some elements are preferentially oxidized during coating preparation. This is liable to occur due to the use of oxygen and compressed air; and also air atmosphere exposure during coating process at high temperature. M.P. Planche et al. [12] reported that the stoichiometry of the oxygen and fuel mixture affects the combustion temperature. The use of lean combustion ratio results in unconsumable oxygen molecules in the flame. It creates an oxidizing atmosphere. This condition and surrounding air severely enhances the oxidation of molten particles. Thus, the deposited coating becomes oxides-rich [12]. Lowering the diffraction peak intensity of FeCr phase with the addition of MCrAlY reveals that the fraction of FeCr phase in the outer coating layer decreases with the increase of MCrAlY concentration. In addition, the presence of  $(Ni,Co)Cr_2O_4$  suggests that some amount of MCrAlY powder is likely to oxidize, even if Co and Ni have lower affinity for the oxygen compared to that of Al and Cr (see Ellingham diagram [25]). In this case, the different in powder size seems to also affect the oxidation of coating powder during coating process. The oxidation of smaller powder is favorable to occur because the smaller particle sizes create larger interfacial areas and increase the number of atoms at the particle interfaces [26]. This results in increasing the oxidation rate of coating powder with the decrease of particle size [27]. The oxygen content in the coatings was affected by in-flight oxidation when the small particles are used and post-impact oxidation when the large particles are used [11]. As mentioned in the experiment, the powder size of MCrAlY is smaller than FeCrAlTiY. Accordingly, MCrAlY powders are likely to oxidize mainly to form  $(Ni,Co)Cr_2O_4$ . Moreover, some Al from MCrAlY may be oxidized to form  $Al_2O_3$ . It undergoes solid state reaction with FeO to form spinel as explained before. While, the oxidation of FeCrAlTiY powders mostly form Fe(Cr,Al)<sub>2</sub>O<sub>4</sub> and FeO as confirmed by XRD analysis. The formation of aforesaid oxidation products appears covering the FeCr phase. As a result, the diffraction peaks of FeCr phase tend to weak with the increase of MCrAlY concentration.

**3.1.2. Microstructure.** Figure 4 shows the BSE-SEM cross-sectional images of FeCrAlTiYcoatings with different composition of MCrAlY as 0, 10, 20, and 30 mass %.

The cross-sectional images of the samples clearly confirm that the coatings were successfully deposited on the surface of carbon steel using a flame spray technique. It can be seen that the coating and substrate interface is clearly defined. The FeCrAlTiY–MCrAlY coatings show a lamellar structure and well adhere to the substrate with a thickness range of approximately  $260-320 \mu m$ . The coatings also contain pores and unmelted or partially melted particles. The presence of pores could be due to the existence of various sizes of unmelted particles which can create porosity in the coatings [14, 20] and act as a source for cracks formation [15]. The pores in the coating layer and interconnected pores at the coating interface can act as short circuit path for cations and/or anions diffusion, reducing protection toward corrosion as well as oxidation. Meanwhile, the difference in coating thickness between each composition as shown in Fig. 4 could be related to the thermal spray process which was operated manually.

According to BSE microstructure images of Fig. 4, mostly, the FeCrAlTiY coatings with different content of MCrAlY consist mainly of three distinguished areas: bright, greyish and darkish areas. In order to further determine the composition of corresponding areas, an EDX elemental point analysis was performed. Figure 5 shows the results of EDX spectrum and point analysis in the corresponding area of FeCrAlTiY coatings with 0 and 30 mass % MCrAlY. In the FeCrAlTiY coating (see Fig. 5a), the bright area (Point 1) is mainly composed of 67.06 at % Fe, 15.83 at % Cr and 12.84 at % Al with a very small concentration of Ti and O, which is suspected to be FeCr phase as detected by X-ray diffraction. The greyish area (Points 2 and 3) and darkish area (Points 4) contains mainly of Fe, Cr, Al and O with varying at % content. In the greyish area, the Fe and O concentrations is



**Fig. 5.** BSE-SEM cross-sectional microstructures and corresponding EDX point analysis in the FeCrAlTiY coatings with (a) 0 and (b) 30 mass % MCrAlY.

higher than Cr and Al, composed of  $Fe(Cr,Al)_2O_4$  and FeO phases as detected by XRD analysis. Meanwhile, in the darkish area is rich in Al and O compared to Fe and Cr, namely Al-rich oxide.

On the other hand, for FeCrAlTiY coating with the addition of 30 mass % MCrAlY (see Fig. 5b), two bright areas with different atomic compositions are found. In point 1, the area contains mainly of 68.09 at % Fe, 15.83 at % Cr and 12.62 at % Al with very small content Ti, Co, Ni and O, suggesting that this area is probably FeCr phase as in the FeCrAlTiY coating without MCrAlY addition. Meanwhile in Point 3, the area is composed of 64.83 at % Fe, 10.97 at % Co, 10.35 at % Ni, and 4.17 at % Cr with some amount of oxygen, confirming that the FeCrAlTiY and MCrAlY powders were already reacted during the deposition process. The difference in element concentration of grey area in Point 2 comprises that the area is mainly

composed of 16.69 at % Fe, 9.24 at % Cr, 11.84 atat % Al and 60.64 at % O with minor elements of Ti, Co, Ni and Y that is suspected to be  $Fe(Cr,Al)_2O_4$  phase. Point 4 shows mainly 12.30 at % Co, 6.81 at % Ni, 12.11 at % Cr, 9.42 at % Al and 57.91 at % O with small content of Fe, Ti and Y that this area is probably  $(Ni,Co)Cr_2O_4$  phase. The dark area (Point 5) is almost similar to that of in FeCrAlTiY coating which is composed of Al-rich oxide (mainly 23.60 at % Al, 6.70 at % Cr, 5.38 at % Fe, 62.53 at % O and minor element of Ti, Co, Ni and Y). It is formed due to oxidation of Al and other elements from FeCrAlTiY and MCrAlY powders of the coating. However, the fraction of this area is smaller compared to the other areas, similarly to that of in the FeCrAlTiY coating. Thus, it may be not detected by XRD analysis as shown in Fig. 3.

The results of SEM-EDX analysis as presented above are in good agreement with the results of X-ray diffraction analysis in Fig. 3. Evidently, some coating



Fig. 6. Mass gain curves of low carbon steel and FeCrAl-TiY coatings with 0, 10, 20, 30 mass % MCrAlY after oxidation in air at 700°C for 8 cycles.

elements of FeCrAlTiY and MCrAlY such as aluminum and chromium which play a significant role in promoting the formation of a protective  $Al_2O_3$  or Cr<sub>2</sub>O<sub>3</sub> scales were preferentially oxidized during coating process. As the MCrAlY content increases, the formation of spinel oxide seems to be increased. For oxidation resistance applications, the formation of oxide during coating process is not expected. This is because the coating becomes depleted with some elements which play a role in promoting the formation of a protective oxide scale and in maintaining the oxide scale protectiveness for long term durability. However, several studies also reported that the spinel oxide can also serves a protection against oxidation and corrosion [13, 22, 23, 28] because the oxygen diffusivity in the spinel oxide is very small [29]. The spinel formation can reduce not only O ions diffusion but also Fe ions and electron free diffusing activities, resulting in high oxidation resistance [23]. Therefore, the formation of spinel oxide in the coating before oxidation at the present study may give a potential beneficial effect as barrier for cation outward diffusion and anion inward diffusion. It may inhibit the growth rate of the oxide scale and improve coating oxidation resistance.

#### 3.2 Coating Characteristics after Exposure at 700° C for 8 Cycles

**3.2.1. Oxidation Kinetic.** The mass gain curves of carbon steel and FeCrAlTiY coatings containing varying amount of MCrAlY after exposure in air at 700°C as a function of cyclic oxidation time are shown in Fig. 6.

The results show that the mass gain of all samples increases with the increase of cyclic oxidation time, attributed to the formation of oxide scale during sample oxidation. According to the oxidation kinetic curve, the uncoated sample shows the highest mass gain (reached 0.757 mg/mm<sup>2</sup>) after 8 cycles exposure

compared to the coated samples from the initial stage of oxidation. This suggests that the uncoated sample has a lowest oxidation resistance. The direct contact of substrate surface to air atmosphere at 700°C leads to the fact that the uncoated sample can be oxidized easily to form oxide layer on the surface of the sample. The scale growth is then controlled by diffusion process of cations and oxygen.

In contrast, the decreasing mass gain of coated sample after oxidation suggests that the FeCrAlTiY-MCrAlY coatings on the surface of carbon steel effectively improve the substrate oxidation resistance. But, their oxidation resistance is compositional dependence. The mass gain curves of Fig. 6 reveal that the total mass gain of FeCrAlTiY coatings containing 0, 10, 20 and 30 mass % MCrAlY after oxidation at  $700^{\circ}$ C for 8 cycles was 0.261 mg/mm<sup>2</sup>, 0.328 mg/mm<sup>2</sup>,  $0.320 \text{ mg/mm}^2$  and  $0.247 \text{ mg/mm}^2$ , respectively. All samples show a quick increase in mass gain in the initial stage of oxidation and then a slow increase in mass gain after 1 cyclic time exposure. The high oxidation rate in the initial oxidation period is due to oxide nucleation and rapid oxide formation, and lower oxidation rate after aforesaid condition is due to oxide scale layer turning into growing stage [2, 22]. Since the oxidation curve follows a parabolic rate low, the oxidation kinetic of coated sample is governed by cation and/or anion diffusion similar to that of metals and alloys [29–31]. No significance difference in mass gain is found in the FeCrAlTiY coatings with 10 and 20 mass % MCrAlY content. The mass gain of both samples is higher compared to the MCrAlY-free coating. While, the FeCrAlTiY-30 mass % MCrAlY coating exhibits lowest oxidation rate, resulting best oxidation resistance.

**3.2.2. Phase Structure.** The X-ray diffraction patterns of uncoated carbon steel substrate and FeCrAl-TiY-MCrAlY coatings after high temperature oxidation test at 700°C in air for 8 cycles are presented in Fig. 7.

The results show that the main phase formed as detected by X-ray diffraction measurement on the carbon steel and FeCrAlTiY coating after exposure at 700°C for 8 cycles is  $Fe_2O_3$  phase. As shown in Fig. 7a,b, however, the intensity distribution of  $Fe_2O_3$  reflection in both samples is somehow different, once the highest intensity of  $Fe_2O_3$  peak at the diffraction angle of about 64.27 deg and the others at 35.59 deg. This different could be due to a preferred growth orientation of  $Fe_2O_3$  in the uncoated sample and FeCrAlTiY coating during the high temperature oxidation test.

The FeCrAlTiY coatings with 10, 20 and 30 mass % MCrAlY after oxidation at 700°C for 8 cycles display similar peak reflection with intensity different. Based on the analysis results, the predominant phase of FeCrAlTiY coatings with different content of MCrAlY detected by X-ray diffraction is the Fe<sub>2</sub>O<sub>3</sub> and Fe(Cr,Al)<sub>2</sub>O<sub>4</sub> phases. It can be seen at diffraction



**Fig. 7.** X-ray diffraction patterns of (a) low carbon steel, FeCrAlTiY coatings with (b) 0, (c) 10, (d) 20 and (e) 30 mass % MCrAlY after oxidation in air at 700°C for 8 cycles.

angle of around 33 deg of Fig. 7c,d,e, the intensity of  $Fe_2O_3$  peak tends to decrease with the increase of MCrAlY content. This suggests that the growth of  $Fe_2O_3$  scale decreases as MCrAlY content increases. It seems that the presence of spinel oxide before oxidation affects the formation and growth of  $Fe_2O_3$  scale, decreasing Fe outward diffusion and oxygen inward diffusion. In addition, it is important to note that the Al<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub> scale is not detected by X-ray diffraction in the FeCrAlTiY–MCrAlY coatings. Mostly Al and Cr elements are already oxidized during coating process as explained earlier.

**3.2.3. Coating Microstrusture.** Figure 8 shows the microstructural evolution of carbon steel and FeCrAlTiY coatings with 0, 10, 20 and 30 mass % MCrAlY after exposure at 700°C for 8 cycles in air.

It can be seen in Fig. 8a that the uncoated sample forms a thick Fe-oxides scale after oxidation at 700°C for 8 cycles, suggesting the carbon steel suffered from high oxidation rate. According to the results of EDX point analysis as shown in Fig. 9, the external oxide layer with the thickness of about 70  $\mu$ m is composed by 37.21 at % Fe and 62.79 at % O. This is closed to the atomic ratio of Fe<sub>2</sub>O<sub>3</sub> as detected by X-ray diffraction





Fig. 8. BSE-SEM cross-sectional microstructures of (a) low carbon steel, FeCrAlTiY coatings with (b) 0, (c) 10, (d) 20 and (e) 30 mass % MCrAlY after oxidation in air at 700°C for 8 cycles.

(see Fig. 7a). Beneath the Fe<sub>2</sub>O<sub>3</sub> scale, the EDX point analysis of Points 2, 3 and 4 as shown in Fig. 9 indicate that the Fe concentration is lower than O. It is near to the atomic ratio of  $Fe_3O_4$ . Accordingly, the oxide scale formed on the carbon steel after exposure at 700°C for 8 cycles is comprised mainly of  $Fe_2O_3$  and  $Fe_3O_4$ . In general, the iron oxidation forms triple oxide layers consisting of  $Fe_2O_3$  in the external layer,  $Fe_3O_4$ beneath the  $Fe_2O_3$  scale and FeO scale on the steel surface [3, 4, 6]. The absence of FeO on the substrate surface indicates that the oxygen potential along substrate/oxide interface is comparatively high [5]. In addition, the cracks are found in the Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> scale interface, in the Fe<sub>3</sub>O<sub>4</sub> scale and at the oxide/steel interface. Previous study reported that the grain boundaries, cracks and pores play a significant role as the transport path for cations and anions diffusion. The outward iron diffusion and inward oxygen diffusion mainly affected the growth of outer and inner oxide layer, respectively [32].

For the FeCrAlTiY coatings with varying concentration of MCrAlY (0, 10, 20 and 30 mass %), the



Fig. 9. BSE-SEM cross-sectional microstructures and corresponding EDX point analysis in the carbon steel substrate after oxidation in air at 700°C for 8 cycles.

MCrAlY-free coating exhibits better coating adherence compared to the other composition, but cracks are mostly formed on the coating surface (oxide layer) as in the FeCrAlTiY coatings with 10, 20 and 30 mass % MCrAlY addition. But, the results show that the cracks in the surface of MCrAlY-free coating is much severe than MCrAlY-containing coatings. On the other hand, it is obvious from Fig. 8 that the FeCrAlTiY coatings with 10 and 20 mass % MCrAlY content are spalling from the surface of low carbon steel, leading to oxidation of low carbon steel and the increase of mass gain of the coated samples (see Fig. 6). Unlike the aforesaid results, the 30 mass % MCrAlY coating exhibits much better coating adherence. Accordingly, the mass gain of the FeCrAlTiY and 30 mass % MCrAlY coatings was governed mostly by cations and anions diffusion in the coating, resulting the lower mass gain compared to the 10 and 20 mass % MCrAlY coatings. The adhesion of the coating and substrate is essential for improving the oxidation resistance of carbon steel and for providing long term durability.

According to the results of EDX elemental analysis as presented in Fig. 10a, the oxide layer of FeCrAlTiY coating (Point 1) is composed mainly by 33.59 at % Fe and 66.26 at % O with a very small concentration of Al and Cr which is confirmed by XRD analysis as Fe<sub>2</sub>O<sub>3</sub>. In the point 2 and 3, the areas are mainly composed of 20.44 at % Fe, 7.15 at % Cr, 8.93 at % Al, 63.03 at % O and 15.95 at % Fe, 10.07 at % Cr, 10.61 at % Al, 62.28 at % O with a small content of Ti and Y, respectively. This is suspected to be Fe(Cr,Al)<sub>2</sub>O<sub>4</sub> as detected by X-ray diffraction analysis. On the contrary, the darker area of Point 4 is rich in Al and O with small amount of Ti, Cr, Fe and Y. This area is almost similar to that of before oxidation.

Meanwhile, for the FeCrAlTiY-30 mass % MCrAlY coating, the external oxide layer is composed mainly of 32.18 at % Fe and 66.94 at % O similar to that of MCrAlY-free coating which forms Fe<sub>2</sub>O<sub>3</sub> scale after exposure for 8 cycles. The grey areas (Points 2 and 4) are composed of two difference compositions. In point 2, it consists of 9.59 at % Fe, 12.49 at % Cr, 13.53 at % Al and 62.62 at % O with a very small concentration of Co, Ni, Ti and Y. Whereas, the area of point 4 contains 22.41 at % Fe, 6.57 at % Cr, 7.33 at % Al, 9.53 at % Co, 7.04 at % Ni and 47.06 at % O with a minor concentration of Ti and Y. Both areas are suspected to be  $Fe(Cr,Al)_2O_4$  and  $(Co,Ni)Cr_2O_4$ , respectively. Point 3 is composed mainly by 81.99 at % Fe. 7.37 at % Co and 3.05 at % Ni with some amount of 0.02 at % Al, 0.24 at % Cr and 7.33 at % O. Al-rich oxide in point 5 consists of 20.55 at % Al, 62.04 at % O, 6.10 at % Fe, 9.70 at % Cr with a small concentration of Ti, Co, Ni and Y.

Based on the results as presented above, it can be summarized that the FeCrAlTiY–MCrAlY coatings did not form a protective  $Al_2O_3$  or  $Cr_2O_3$  scales on its surface. This is attributed to that the Al or Cr elements in the powders were mostly oxidized during coating process to form spinel oxides. Consequently, the coatings become depleted in Al and Cr. The insufficient amount of those elements inhibits the protective oxide formation. Additionally, it is interesting to note that Fe<sub>2</sub>O<sub>3</sub> scale is formed in the outer layer of FeCrAlTiY coatings containing varying amount of MCrAlY. The presence of spinel oxide before oxidation and the formation Fe<sub>2</sub>O<sub>3</sub> scale after exposure at 700°C for 8 cycles strongly suggest that the aforesaid evidence allows the Fe ions to diffuse outwardly through spinel or defect in the coating and oxidize in the outer layer, forming



**Fig. 10.** BSE-SEM cross-sectional microstructures and corresponding EDX point analysis in the FeCrAlTiY coatings with (a) 0 and (b) 30 mass % MCrAlY after oxidation in air at 700°C for 8 cycles.

Fe<sub>2</sub>O<sub>3</sub> scale. D. Lussana et al. [33] also reported that during scales growth, the spinel type oxide becomes progressively richer in iron, up to the transformation in hematite (Fe<sub>2</sub>O<sub>3</sub>) [33]. However, the decrease in peak intensity of Fe<sub>2</sub>O<sub>3</sub> at around 33 deg of Fig. 7c,d,e reveals that the Fe outward diffusion is likely to decrease with the increase of MCrAlY content. Accordingly, it is important to note that the protection of FeCrAlTiY–MCrAlY coatings prepared by a flame spray technique against cyclic oxidation at high temperature is provided by Fe<sub>2</sub>O<sub>3</sub> and spinels formation.

Meanwhile, there are several factors that contribute to the scale cracking and coating adherence or spallation in this study: pore existence [15], growth stress of oxide layer and thermal stress [2, 3, 5, 6, 13, 32, 34, 35] during cyclic oxidation test. As shown in the results of coating microstructure before oxidation, the coating is composed of metallic and oxide phases and also contains some pores. The existence of pores in the coating layer can create or generate the cracks. This results in the decrease of coating adherence. Moreover, the pores at the coating interface tend to become transport path for oxidant and corrodents, reducing its oxidation and corrosion resistance. Under thermal cyclic condition, high thermal stress was generated during high heating and cooling in the coating (between oxide phase and metallic phase) and at the coating/substrate interface due to the difference in thermal expansion coefficient [3, 6, 11, 35]. This turns into oxide cracking mostly in the external oxide layer of FeCrAlTiY-MCrAlY coatings, at the coating interface in 30 mass% MCrAlY coating and coating spallation in the 10 and 20 mass % MCrAlY coatings. In addition, the growth stress of oxide layers enhanced the cracks initiation and propagation. The presence of cracks in the coating and coating/substrate interface can act as transport parts for oxygen inward diffusion

and/or cation outward diffusion. This can accelerate the degradation of coating and substrate. However, the reason for why the FeCrAITiY coatings with 10 and 20 mass % MCrAIY spalled out from the coating surface and 30 mass % MCrAIY coating more resists to coating exfoliation still need to be understood. The results as presented above show that the FeCrAITiY-30 mass % MCrAIY coating after exposure at 700°C for 8 cycles exhibits the lowest mass gain associated with best oxidation resistance.

#### 4. CONCLUSIONS

FeCrAlTiY coatings containing various amounts of MCrAlY as 0, 10, 20, 30% by mass were prepared by a flame spray technique on the surface of low carbon steel. The resistance of coated and uncoated samples against oxidation at 700°C for 8 times was investigated. Based on the results obtained the following conclusion can be drawn:

1. Some elements of FeCrAlTiY–MCrAlY coatings were already oxidized during flame sprayed deposition, forming oxide scales of  $Fe(Cr,Al)_2O_4$ , (Co,Ni)Cr<sub>2</sub>O<sub>4</sub> and FeO.

2. Carbon steel experienced a high oxidation rate after exposure at 700°C for 8 cycles, forming  $Fe_2O_3$  and  $Fe_3O_4$  scales on its surface.

3. On the contrary, even if a protective  $Al_2O_3$  or  $Cr_2O_3$  scales is not formed after 8 times exposure, the FeCrAlTiY–MCrAlY coatings effectively improve the oxidation resistance of carbon steel due to the formation of spinel oxides and Fe<sub>2</sub>O<sub>3</sub> scale.

4. The FeCrAlTiY coating with 30 mass % MCrAlY exhibits lowest mass gain among other composition associated with an excellent oxidation resistance.

#### ACKNOWLEDGMENTS

This work was financially supported by Program Unggulan 2018 of Indonesian Institute of Sciences. Characterization facilities provided by Research Center for Physics, Indonesian Institute of Sciences were gratefully acknowledged. The authors are grateful to Mr. Ciswandi and Mr. Edi Setiawan for technical support and fruitful discussion.

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# The effect of FeMn and FeB additive on hematite $(\alpha\text{-}\text{Fe}_2\text{O}_3)$ and their characterization

To cite this article: M Ginting et al 2019 J. Phys.: Conf. Ser. 1191 012035

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## The effect of FeMn and FeB additive on hematite (α-Fe<sub>2</sub>O<sub>3</sub>) and their characterization

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Abstract. In this study, the mineral material addition of FeMn and FeB to the hematite ( $\alpha$ - $Fe_2O_3$ ) by varying each mass concentration of 0, 4, and 8 wt.% have been prepared by powder metallurgy method. The mixing process of the powder was done by high energy milling (HEM) for 1 h. Then, the powders were calcined at temperature of 1000 °C for 2 h. The Effect of FeMn and FeB additives on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> causes the increasing of the particles diameter. The increasing of FeMn additive increases the powder density of material, but the addition of FeB decreases it. The material of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>with FeMn additive has dominant phases of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and the minor phases of MnO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>. The material of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with FeB additive has two phases as magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). The magnetic properties of a  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material with FeMn and FeB additives decrease the saturation value and coercivity.

#### **1. Introduction**

Material for magnetic is important because it is widely applied in the industries, including automotive. Indonesia has an abundant source of raw materials; one of them is iron sand. According to Widanarto [1] the form of iron sand that naturally occurs in mineral is ferrous ferrite (Fe<sub>3</sub>O<sub>4</sub>). By the heating processes at elevated temperatures, the resulting of magnetite phase (Fe<sub>3</sub>O<sub>4</sub>) changed into hematite (α- $Fe_2O_3$  [2]. This change is followed by the changes in atomic arrangement and its magnetic properties [3]. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) materials tend to stable at high temperature in comparison with magnetite  $(Fe_3O_4)$  [4]. Therefore hematite is more often used as a raw material for synthesizing ferrite magnets [5]. The ferrite magnet has strong mechanical properties, not easily corrode, high electromagnetic performance, excellent chemical stability, low coercivity, and moderate saturation magnetization [6, 7]. The hematite material  $(\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is an oxide that is widely used in various applications. Some applications are gas sensors, catalyst agents, lithium ion batteries [8], photoelectrochemical [9], biomedical devices, pigments, [10] and many others. Several methods are used for the preparation of α-Fe<sub>2</sub>O<sub>3</sub> such as sol gel, force hydrolysis, microemulsion, precipitation, direct oxidation, thermal decomposition, sonochemical, hydrothermal, solvothermal, and electrochemical [11, 12].

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International Symposium on Frontier of Applied Physics IOP Publishing IOP Conf. Series: Journal of Physics: Conf. Series **1191** (2019) 012035 doi:10.1088/1742-6596/1191/1/012035

Ferro boron (FeB) is used as an additive for steel and iron because it can improve material mechanical properties and also the price is relatively cheap. Recently, FeB attract attention as a magnetic additive, one of which is the manufacture of NdFeB permanent magnets. FeB is a metal alloy composed of iron and boron with boron content ranging from 10 to 20%. Iron is widely used in the production of permanent magnets due to its high magnetic properties, while boron is hard and diamagnetic.

Ferro manganese (FeMn) has cubic structure and includes as soft magnetic. Manganese has a high melting temperature which is 1244 °C, so it can retain at high temperature of such heat treatment. Therefore, the addition of FeMn into barium hexaferrite can decrease its magnetic properties.

In the previous study, Shen et al. [13] modified the nanocomposite Fe<sub>3</sub>O<sub>4</sub>-FeB and produced lower magnetic properties than Fe<sub>3</sub>O<sub>4</sub>. In other research, Lee [14] also synthesized Mn doped Fe<sub>2</sub>O<sub>3</sub> and the magnetic properties decrease with increasing Mn. In this preliminary research, we apply FeM and FeB as doping to determine the properties within soft magnetic. FeM and FeB is aplied due to have low magnetic properties. From this study, with addition of FeM and FeB into Fe<sub>2</sub>O<sub>3</sub>, it is expected to produce nanocomposite Fe<sub>2</sub>O<sub>3</sub> with lower magnetic properties. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is synthesized into pellet with the addition of iron manganese and iron boron (FeB) was carried out by powder metallurgy method and followed by the calcination process. Powder metallurgy is considered due to its easy and large scale applications.

#### **2. Experimental Methods**

FeMn and FeB additives were raw materials which were obtained from the nature with bulk form. Then, it was ground into powders to pass 200 mesh sieve. Furthermore, each of FeMn and FeB powders were added to the main raw material of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and milled using the high energy milling (HEM) shaker mill PPF-UG for 1 h. The variation of FeMn and FeB additives were 4 and 8 wt% which were added to hematite powder ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). After milling, the powder was measured to find the powder density by pycnometer and its particle distribution was analyzed using the particle size analyzer (PSA). The powders were calcined at 1000°C for 2 h. Then the microstructure was analyzed by the X-ray diffraction (XRD - Rigaku SmartLab, Cu-k $\alpha$  1.5406). While the magnetic properties were analyzed by using the vibrating sample magnetometer (VSM - Electromagnetic, 250).

#### 3. Results and Discussion

The particle size distribution of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is shown in figure 1. While the distribution analysis and particle size of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> after adding FeMn and FeB additives are shown in figure 2. From figure 2, it is clearly seen that the particle size differences based on the cumulative value diameter at statistical positions 10, 50, and 90%. The particle size distribution obtained is heterogeneous with the presence of peaks formed.



Figure 1. Distribution histogram of mean particle diameter of α-Fe<sub>2</sub>O<sub>3</sub>.

IOP Conf. Series: Journal of Physics: Conf. Series 1191 (2019) 012035 doi:1

doi:10.1088/1742-6596/1191/1/012035



**Figure 2.** Distribution histogram of mean particle diameter of (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> + 4% FeMn, (b)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> + 8% FeMn, (c) $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> + 4% FeB, and (d)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> + 8% FeB.



**Figure 3.** The Correlation of powder density and mean diameter of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) with an addition of (a) FeMn, and (b) FeB.

The correlation between powder density and mean diameter of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> after adding FeMn and FeB are shown in figure 3. From figure 3, it can be seen that the effect of the addition of FeMn and FeB causing the mean diameter of particle tends to increase. It means that the milling effect for 1 h with high energy milling (HEM) has not been able to reduce the particle size of additives, where  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particle is around 1.7 µm. The powder density values tend to decrease with the addition of FeB additive, while the powder density tends to increase with the addition of FeMn additives.

Thus, it can be seen that the correlation between the powder densities to the mean diameter of FeMn addition is proportional, but inversely proportional for the addition of FeB. The density value of

FeMn, FeB, and  $\alpha$ -Fe2O3 is about 7.3, 4, and 5.27 g/cm<sup>3</sup>, respectively. From those density values, the FeMn is higher than  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Thus, density of sample increases with more addition of FeMn. Conversely, the powder density tends to decrease with the addition of FeB. The higher density of FeMn doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> than FeB doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can be explained due to the hardness value of FeMn is higher than FeB. From this result, the number of density is strongly influenced by the heat treatment and material composition.

The phase analysis by using XRD of hematite powder ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) after added by the FeMn and FeB are shown in figure 4. The obtained diffraction pattern are for (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, FeB, and FeMn as raw material, and (b) the mixing of 4% FeMn +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and the mixing of 8% FeB +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> additive after calcination at1000°C for 2 h.

From figure 4 (a) the XRD analysis result of FeMn material shows the major peaks of FeMn phase. FeMn has a cubic structures and lattice parameters of a = 3.668 Å. In the diffraction pattern of FeB, it has single phases with lattice parameter of a = 4.053 Å, b = 5.495 Å, and c = 2.946 Å. While diffraction pattern of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has a single phase which has a rhombohedral structure with lattice parameters of a = b = 5,032 Å and c = 13,733 Å. The diffraction pattern in figure 4 (b) is the diffraction of 4% FeMn +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and 8% FeB +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The obtained diffraction pattern shows three phases, which has  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as the dominant phase and the two others phases are MnO<sub>2</sub> and Fe<sub>2</sub>(BO<sub>3</sub>)O phases.



**Figure 4.** X-ray diffraction pattern of raw materials (a) FeMn, FeB, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and (b)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> added 4% FeMn and 8% FeB with calcination at 1000 °C for 2 h.

The magnetic properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with an additive variation of FeMn and FeB before and after calcination is shown in figure 5. In table 1, it can be seen that the value of saturation, remanence magnetization, and coercivity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> are 0.68 emu/g, 0.12 emu/g, and 372.31 Oe, respectively. These values are low because the basic properties of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material at room temperature are antiferromagnetic [15], so that this material will have very little response to the magnetic field. While for samples with 4 and 8% FeMn addition, it shown that the value of saturation, remanence magnetization, and coercivity are close resemblance as shown in figure 5 (a). These values are much greater than the value of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material, but for sample with 4 and 8% FeMn addition after calcination at 1000°C for 2 h, its magnetic properties decrease to a quite low value as shown in figure 5 (b). This can be explained due to the addition of FeMn resulting the  $MnO_2$  phase as can be seen from the XRD results. Although the dominant phase in the sample is  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> which has antiferromagnetic properties, the appearance of  $MnO_2$  affects significantly its magnetic properties. The magnetic properties of a material are also influenced by other factors such as the degree of crystallinity, particle size and the presence of secondary phase effects [16]. Furthermore, the same phenomena shown on the sample with the addition of 4 and 8% of FeB followed by the calcination at 1000°C for 2 h. It is also found that due to the addition of FeB, it also forms the new phase of  $Fe_2(BO_3)$  (figure 2 (b)) that decreases the magnetic properties. From the result, prior to calcination, magnetic properties of each

sample is influenced by  $Fe_2O_3$  and the additive, but after the calcination nanocomposite  $Fe_2O_3$ -FeMn produced  $MnO_2$  and nanocomposite  $Fe_2O_3$ -FeB produced  $Fe_2(BO_3)$ . Both  $Fe_2(BO_3)$  and  $MnO_2$  have antiferromagnetic behavior, therefore their magnetic properties decrease.



**Figure 5**. Magnetic properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with additive variations of FeMn: (a) before and (b) after calcinations; and variations of FeB: (c) before and d) after calcinations.

**Table 1.** Magnetic properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with additive variations of FeMn, before and after calcined at 1000°C for 2 h.

Composition of -	В	efore Calcinatio	on	After Calcination		
	σs	σr	jHc	σs	$\Sigma r$	jHc
Telvin (wt. 70)	(emu/g)	(emu/g)	(Oe)	(emu/g)	(emu/g)	(Oe)
0	0.68	0.12	372.31	19.76	10.31	1430.96
4	1.09	0.18	352.04	1.55	0.48	380.98
8	1.02	0.17	330.94	1.45	0.54	312.91

**Table 2.**Magnetic properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>with an additive variation of FeB, before and after calcined At 1000°C for 2 h.

Composition of FeB (wt.%)		Before Calcina	ation		After Calcination		
	σs	σr	jHc	σs	Σr	jHc	
	(emu/g)	(emu/g)	(Oe)	(emu/g)	(emu/g)	(Oe)	
0	0.68	0.12	372.31	19.76	10.31	1430.96	
4	2.32	0.29	293.92	0.38	0.08	1326.18	
8	4.87	0.48	288.50	0.42	0.12	1350.24	

#### 4. Conclusions

Powder hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) with the addition of FeMn and FeB additives derived from natural raw materials has been successfully made with powder metallurgy method. Then samples were calcinated at the temperature of 1000°C for 2 hours. The analysis showed that the powder with the Fe<sub>3</sub>Mn<sub>7</sub> addition has a dominant phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and two new phases of MnO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>. The result of powder

International Symposium on Frontier of Applied Physics

IOP Conf. Series: Journal of Physics: Conf. Series 1191 (2019) 012035 doi:10.1088/1742-6596/1191/1/012035

density measurement showed that the optimum value was obtained for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> sample with 8% wt Fe<sub>3</sub>Mn addition. This material is classified as a hard magnet with magnetization value of saturation, remanent and coercivity of 24.0 emu/g, 10.3 emu/g and 571.8 Oe. The effect of 8 wt.% FeB addition on hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) material before calcination resulting the decrease of the coercivity value from 372.19 Oe to 285.06 Oe. The influence of calcination temperature 1000 °C for 2 h causes increasing of the grain growth and magnetic properties. While the effect of FeB addition at 0, 4, and 8 wt.% after calcination tends to convert the sample into soft magnetic with coercivity values of 1450, 1220 and 1180 Oe

#### Acknowledgements

The authors would like to thank the Center for Research Physics of Indonesian Institute of Sciences (P2F LIPI) for the use of facilities and research funds that has been given.

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To cite this article: P Sebayang et al 2019 J. Phys.: Conf. Ser. 1191 012034

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## The influence of sintering temperature on characteristic of ceramics based on bentonite, glass bead and alumina

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Abstract. Bentonite, glass bead, and  $Al_2O_3$  based fine ceramics with variation of sinter temperatures (900, 1000, 1100, and 1200°C) have been prepared by powder metallurgy method. The preparation process of raw materials starts from the mixing of 35 wt% powder bentonite, 35 wt% glass bead, and 30 wt% alumina using High Energy Milling (HEM). After that, the powders are compacted with 80 kgf/cm<sup>2</sup> into pellets. The samples are dried using oven at 100°C for 24 hours. Characterization tested includes physical properties (density, porosity, water absorption, and hardness), microstructure by using SEM and phase analysis by using XRD (X-Ray Diffraction). The results show that the phase formed are the major phase of albite  $(Al_2NaO_8Si_3)$  and quartz  $(SiO_2)$ , while the corundum  $(Al_2O_3)$  and nepheline  $(AlNaO_4Si)$  are minor phases. The result of analysis shows that bulk density and hardness value tends to increase, while porosity and water absorption tend to decrease along with increasing sinter temperature. The optimum condition was reached at  $1100^{\circ}$ C with bulk density = 2.43 g/cm<sup>3</sup>, porosity = 1.91%, water absorption = 0.8, and hardness = 878.29 HV.

#### 1. Introduction

Ceramic materials based on oxide compounds like Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, MgO, and TiO<sub>2</sub> have advantages such as high melting point, hard, refractory (high temperature resistant), strong, and insulators [1, 2]. Aluminum oxide (alumina) is a chemical compound of aluminum and oxygen, with the chemical formula of Al<sub>2</sub>O<sub>3</sub>. This material melts at a temperature of 2050°C and maintains its strength even at a temperature of 1500 to 1700 °C [3, 4]. Alumina is often used in various applications because of its strict physical and chemical properties such as very high strength, extremely hard, good electrical insulation, high heat resistance, high overtime temperature, high abrasion, and corrosion resistance [5, 6].

Silica or silicon oxidation has a chemical formula  $SiO_2$  formed from silica and oxygen atoms. Silica can be applied in various mechanical electronics and can be made into ceramic materials. Silica

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compounds contained in nature are crystalline structures, which as compounds derived from synthetics are amorphous. Silica can be found in three crystalline forms that is quartz, tridymite, and cristobalite [7, 8].

The sintering process is a process of compacting powder material by forming grain boundaries bonding between powder constituents. The intercellular bonding occurs due to heating and sintering temperature set under the melting temperature of the constituent particles. In the sintering process, compacted materials occur because of the formation of bonds between particles [9].

In this experiment, the research will be focused on influence of sintering temperature variations on the characteristics of ceramics based on alumina, bentonite, and glass bead. Samples in the pellet form are sintered at 900, 1000, and 1100°C [10-12]. Characterization is performed to find out crystallinity, density, hardness, and microstructures.

#### 2. Experimental Methods

The preparation process began with the preparation of Al<sub>2</sub>O<sub>3</sub> (30 wt%), glass bead (35 wt%), and bentonite (35 wt%) materials [13]. All the materials were mixed and milled with an aquadest medium by using HEM (High Energy Milling) for 2 hours. The milled powder was then heated to 100°C for 24 hours. The fine powder was put into beaker glass and was added 5 wt% of epoxy resin as adhesive. The mixture was sintered at the temperature of 900, 1000, and 1100°C for 4 hours, which were named as samples A, B and C, respectively. The characterization includes particle size distribution by using particle size analyzer (PSA Cilas-1190), phase analysis with X-ray diffraction (XRD Rigaku Smart Lab type,  $\lambda = 1.5418$  Å), microstructural analysis with scanning electron microscopy (SEM Hitachi SU -3500), and hardness analysis with microhardness tester (MHT LECO LM-100AT)

#### 3. Results and Discussion

The powder particles size distribution of bentonite, glass beads, alumina, and mixed powder material are shown in figure 1. The original particle size of bentonite, glass beads, and alumina is 16.88, 516.97, and 105.86  $\mu$ m. After milling for 2 hours, the average particle size is 4.27  $\mu$ m, as shown figure 1. From figure 1, it shows that the particle size is less homogeneous distribution. For 10% cumulative distribution, there is a particle diameter about 0.2  $\mu$ m which are part of the bentonite. While particle diameter between 0.8 - 20  $\mu$ m is the largest part of alumina and glass beads. From previous study, for a similar composite has similar range of silica and alumina diameter is around 6–50  $\mu$ m [14].

The bulk density and porosity of samples A, B, and C which was sintered at the temperature of 900, 1000, and 1100 ° C for 4 hours respectively were measured by using Archimedes method (ASTM C373-88) [15, 16]. From Figure 2, it can be seen that the density value is inversely proportional to the porosity. The higher of sintering temperature increases the density and decreases the porosity of the samples. As a result of sintering, densification process was occurred and resulted in less number of pores [17]. The highest density and porosity value are on sample C, with the value about 2.43 g/cm<sup>3</sup> and 1.92%, respectively because the phases of corundum and quartz are occurred as can be seen in figure 3.

The result of XRD analysis is shown in figure 3. From figure 3, it shows that in samples A and B have identical phase. There are 4 phases of albite  $(Al_2NaO_8Si_3)$ , corundum  $(Al_2O_3)$ , nepheline  $(AlNaO_4Si)$ , and quartz  $(SiO_2)$  [18]. While on sample C, it shows that the peak of nepheline and quartz are reduced while albite's peak is sharper. This suggests that the effects of quartz and nepheline change to form the albite phase.



**Figure 1.** Particle size distribution of (a) bentonite, (b) glass beads, (c) alumina and (d) mixed sample after milling for 2 hours.



Figure 2. The influence of various sintering temperature to bulk density and porosity of ceramic based on bentonite, glass bead, and alumina.





**Figure 3.** X-ray diffraction pattern of ceramic based on bentonite, glass bead, and alumina with various sintering temperatures.

**Figure 4.** SEM images of ceramic based on bentonite, glass bead, and alumina after calcination of 900°C (sample A).

Sample morphological analysis with SEM is shown in figure 4. In this research, the morphology of sample A is analyzed by SEM. From figure 4, it shows that in higher of sintering temperature, pore of the sample is getting smaller. This is consistent with the results of its density and porosity measurements. The higher of sintering temperature causes the higher of density but the porosity tends to shrink [14]. From the result of SEM-EDX, there are elements of O, Na, Mg, Al, Si and Ca in the sample A. The SEM-EDX results related to XRD results with albite (Al<sub>2</sub>NaO<sub>8</sub>Si<sub>3</sub>), corundum (Al<sub>2</sub>O<sub>3</sub>), nepheline (AlNaO<sub>4</sub>Si), and quartz (SiO<sub>2</sub>) phases. Even though, there does not find an element of Ca in the phase from XRD results. This is due to Ca as a minor content in the amorphous form which Ca is part of bentonite [11, 15].

The hardness test to finding the influence of sintering temperature on ceramics based on bentonite, alumina and glass bead is measured by using Vickers method. The hardness test results are shown in figure 5. From figure 5, it can be seen that the value of hardness increases with the increase of sintering temperature. In this study, the highest hardness was obtained in sample C with the hardness value of 878.29 HV. The hardness degree of material is strongly influenced by the density and porosity. The higher the density of a sample increases the hardness of the sample. The result of the hardness in these samples is corresponding to density and porosity of the samples. Sample C that has higher density and lower porosity has higher hardness and vice versa. Meanwhile, as the result of diffraction pattern, is albeit which more hardness than nepheline and the dominant phase in component of sample C, so it caused sample C to be the hardest among others.

#### 4. Conclusions

It has been made fine ceramic based on alumina, bentonite, and glass beads with a sintering temperature of 900, 1000 and 1100°C for 4 hours. The characterization results show the sample density increases, while the porosity decreases with the increase of sintering temperature. The result of phase analysis shows that there are 4 main phases: albite (Al<sub>2</sub>NaO<sub>8</sub>Si<sub>3</sub>), corundum (Al<sub>2</sub>O<sub>3</sub>), nepheline (AlNaO<sub>4</sub>Si), and quartz (SiO<sub>2</sub>). The value of sample hardness increases with the increase of sintering temperature. The optimum sample was obtained at the sintering temperature of 1100°C (sample C) with density, porosity, and hardness about 2.43 g/cm<sup>3</sup>, 1.92%, and 878.29 HV. Therefore, the best composition for fabrication of fine ceramic based on alumina, bentonite, and glass beads is the sample C.

**Table 1.** Element analysis result of ceramic based on bentonite, glass bead, and alumina after calcination at 900°C (sample A).

Element	Weight%	Atomic%
0	64.64	76.05
Na	2.28	1.87
Mg	1.38	1.07
Al	13.89	9.69
Si	14.81	9.92
Ca	3.00	1.41
Totals	100.00	100.00



Figure 5. The influence of various sintering temperature to hardness of ceramic based on bentonite, glass bead, and alumina.

#### Acknowledgements

The authors would like to thank the Center for Research Physics of the Indonesian Institute of Sciences (P2F LIPI) Puspiptek Area, South Tangerang, for the use of facilities and research funds that have been given.

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