

Cr-Al coatings on low carbon steel prepared by a mechanical alloying technique

A I J Hia¹, T Sudiro^{2,*}, D Aryanto² and K Sebayang¹

¹Postgraduate Program, Faculty of Mathematic and Natural Science, University of Sumatra Utara, Sumatera Utara, 20155 Indonesia.

²Research Center for Physics, Indonesian Institute of Sciences, Kawasan Puspiptek Serpong, 15310 Indonesia.

*e-mail: toto.sudiro@lipi.go.id

Abstract. Four different compositions of Cr and Al coatings as Cr₁₀₀, Cr_{87.5}Al_{12.5}, Cr₅₀Al₅₀, and Al₁₀₀ have been prepared on the surface of low carbon steel by a mechanical alloying technique. The composition of each powder was milled for 2 hour in a stainless steel crucible with a ball to powder ratio of 10:1. Hereafter, the Cr-Al powder and substrate were mechanical alloyed in air for 1 hour. Heat treatment of coated sample were carried out at 800°C in a vacuum furnace. In order to characterize the phase composition and microstructure of the coating before and after heat treatment, XRD and SEM-EDX were used. The results show that Cr, Cr-Al or Al coatings were formed on the surface of low carbon steel. After heat treatment, new phases and interdiffusion zone were formed in the coating and at the coating/steel interface, depending on the coating composition.

1. Introduction

Carbon steels have been widely used for wide range applications due to the cost consideration. Mostly, however, it shows low oxidation resistance at high temperature [1]. Accordingly, a protective coating is required to improve their oxidation resistant.

Al₂O₃ former as FeAl [2], NiAl [3], TiAl [4] and Cr₂O₃ former as NiCr [5] have been applied as coating on the samples surface to improve its oxidation resistance. The formation of a protective oxide layer of alumina or chromia on the coating surface can play a role to retard the inward diffusion of oxygen. It is generally agreed that Al and Cr are important elements for improving the high temperature oxidation resistance of alloys and coatings. However, far too little attention has been paid to Cr-Al coating which can act as reservoir for the formation of Al₂O₃ and/or Cr₂O₃ on the coating surface at high temperature.

Several techniques as high velocity oxygen fuel (HVOF) [6], air plasma spraying (APS) [7], physical vapor deposition (PVD) [4] and mechanical alloying (MA) [8-12] have been used to deposit coatings on the surface of materials. It is known that mechanical alloying is a new technique which can be utilized to produce intermetallic coatings on steel [8] and nanostructure coating on various metal surfaces [9]. In this technique, the coatings formation on the sample surface is caused by the ball and powder particles collision on the sample surface. Thus, several factors as coating composition, ball and powder ratio, and rotation speed or oscillation frequency will affect the establishment of coatings on the surface of sample. From the view point of coating development, how to produce uniform coating structure becomes particularly important.



Based on the aforementioned conditions, in this study, Cr-Al coatings with varying composition were prepared by a mechanical alloying technique. Heat treatment was also performed in order to improve or refine the coating structure. Metallographic characterizations of the coating before and after heat treatment were studied by mean of XRD and SEM-EDX.

2. Experimental Procedures

Commercial low carbon steel with an approximate dimension of 10 x 8 x 3 mm was used as substrate in this study. For the coating deposition, the alloy surface was polished down by using various grades of SiC papers for up to #1200. The specimen was then ultrasonically cleaned in an ethanol solution. The nominal composition of powder for coating was presented in Table 1.

Table 1. Nominal composition of Cr-Al coatings (in at%).

Coating	Nominal Composition (at%)	
	Cr	Al
Al ₁₀₀	-	100
Cr ₅₀ Al ₅₀	50	50
Cr _{87.5} Al _{12.5}	87.5	12.5
Cr ₁₀₀	100	-

The deposition of coating on the surface of low carbon steel was performed in a shaker mill by a mechanical alloying technique. For each composition, the powders were milled for 2 h in the steel crucible by using high speed shaker mill. The steel balls and powder ratio used in this study are 10 to 1. After 2 h milling, the substrate of low carbon steel was charged into the steel crucible containing milled powder and mechanically alloyed for 1 h. The deposition of coating on the surface of low carbon steel occurs due to the collisions between balls and powder on the substrate of low carbon steel. After Cr-Al coatings deposition, the specimens were then heat treated in a vacuum furnace of 5.6 Pa for 2 h at 800°C.

X-ray diffraction (XRD) and scanning electron microscope equipped with energy dispersive X-ray spectrometer (SEM-EDX) were used to characterize the phase composition and microstructure of coating before and after heat treatment, respectively.

3. Results and Discussion

3.1. Phase composition and microstructure of the Cr-Al coatings before heat treatment

X-ray diffraction patterns of Al₁₀₀, Cr₅₀Al₅₀, Cr_{87.5}Al_{12.5} and Cr₁₀₀ coatings before heat treatment are shown in Figure 1. The XRD analysis shows reflections of Al and Cr in the Al₁₀₀ and Cr₁₀₀ coatings as shown in Figures 1(a) and (d), respectively with some reflection peaks of Fe from substrate of low carbon steel. Meanwhile in the Cr₅₀Al₅₀ and Cr_{87.5}Al_{12.5} coating, both of Cr and Al reflections can be clearly seen in Figures 1 (b) and (c). The results of XRD characterization reveal that Cr-Al coatings were successfully deposited on the surface of low carbon steel.

The cross-sectional BSE images of Al₁₀₀, Cr₅₀Al₅₀, Cr_{87.5}Al_{12.5} and Cr₁₀₀ coatings before heat treatment are shown in Figures 2 (a), (b), (c) and (d), respectively.

The thickness of Al coating, as shown in Figure 2 (a) is about 30 µm. EDX characterization confirms small Fe particles in the Al-matrix which probably come from the steel substrate or milling media. During the powder milling or coating deposition, the collisions between steel balls, crucible and sample may lead to steel spallation. From Figure 1 (a), it can also be seen that the Al coating exhibits good adherence to the alloy substrate. In the Cr-Al coatings (Figures 2 (b) and (c)), the coatings are composed of grey particles of Cr and dark area of Al with the coating thickness of about 60-80 µm. The Cr-particles in the Cr₅₀Al₅₀ coating are smaller and more uniformly distributed compared to in the Cr_{87.5}Al_{12.5} coating. For Cr₁₀₀ coating (Figure 2(d)), the thickness and microstructure of the coating are uneven. A relatively dense structure can be observed on the surface of low carbon steel and porous structure is found near to the surface of the coating. In addition, the

SEM image also shows that the sample surface is rough. This could be related to the fact that Cr hardness ($H_v = 1060$ MPa) is higher compared to the Fe hardness ($H_v = 608$ MPa). Accordingly, the deposition of Cr particles on the steel surface strongly affects the morphology of sample surface.

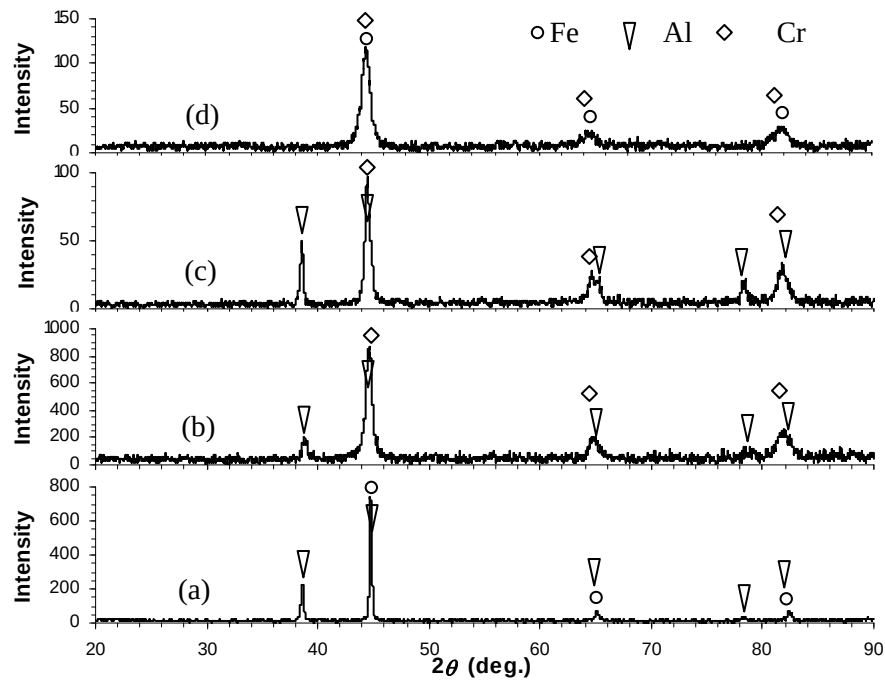


Figure 1. X-ray diffraction patterns of (a) Al_{100} , (b) $Cr_{50}Al_{50}$, (c) $Cr_{87.5}Al_{12.5}$ and (d) Cr_{100} coatings before heat treatment.

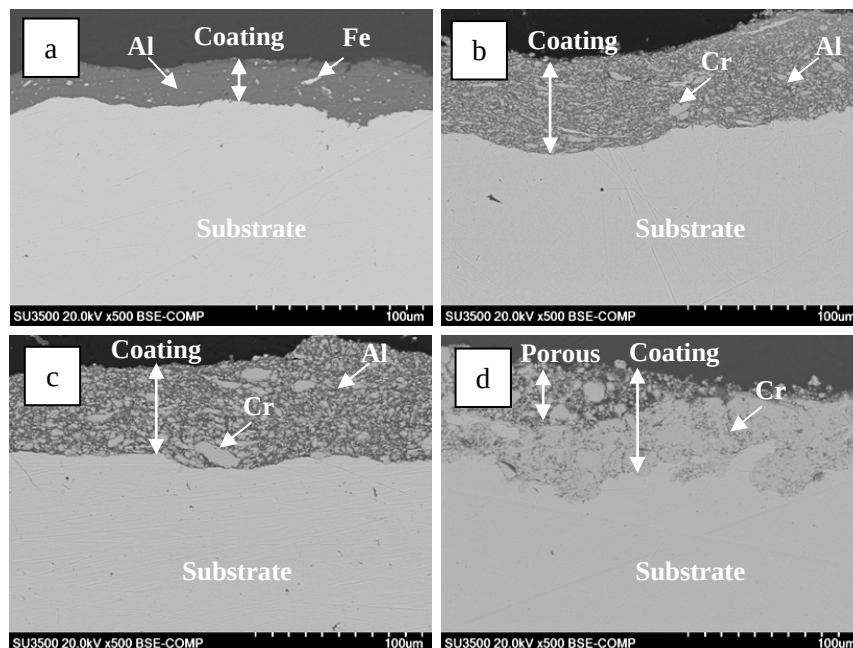


Figure 2. Cross-sectional BSE images of (a) Al_{100} , (b) $Cr_{50}Al_{50}$, (c) $Cr_{87.5}Al_{12.5}$ and (d) Cr_{100} coatings before heat treatment.

3.2. Phase composition and microstructure of the Cr-Al coatings after heat treatment at 800°C

Figure 3 shows the X-ray diffraction patterns of Al₁₀₀, Cr₅₀Al₅₀, Cr_{87.5}Al_{12.5} and Cr₁₀₀ coatings after heat treatment at 800°C for 2 h.

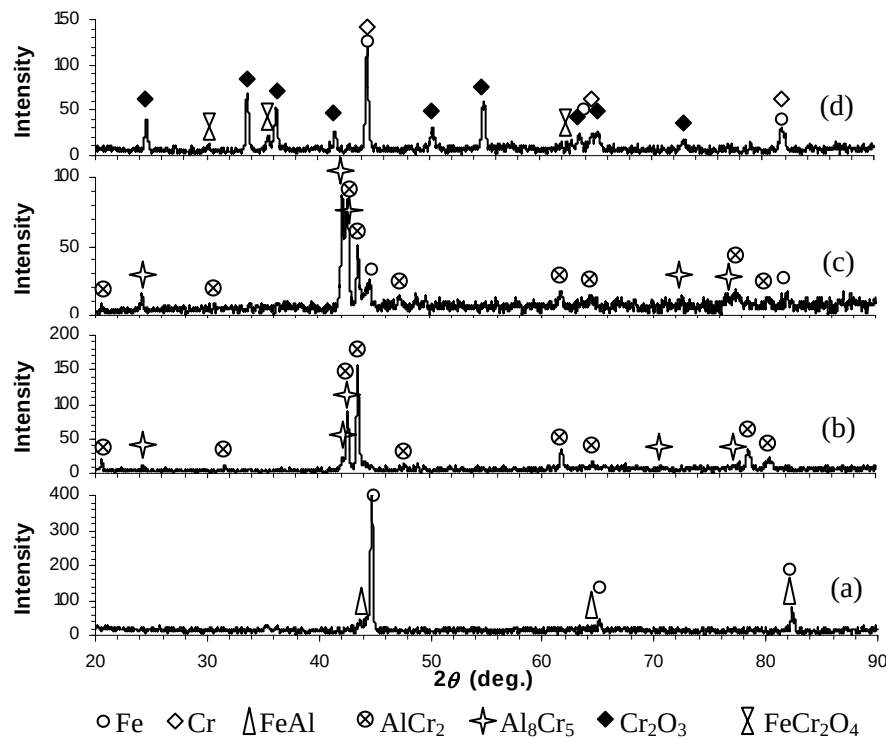


Figure 3. X-ray diffraction patterns of (a) Al₁₀₀, (b) Cr₅₀Al₅₀, (c) Cr_{87.5}Al_{12.5} and (d) Cr₁₀₀ coatings after heat treatment at 800°C for 2 h.

XRD patterns, as shown in Figure 3 indicate that the coating structure after heat treatment is depended on the coating composition. In the Al₁₀₀ coating, FeAl phase is formed after heat treatment at 800°C for 2 h. In the Cr₅₀Al₅₀ coating, the coating is composed mainly of AlCr₂ phase with small reflections of Al₈Cr₅ phase. As Cr concentration increases, XRD characterization reveals that Al₈Cr₅ reflection in the Cr_{87.5}Al_{12.5} coating is higher and AlCr₂ reflection in the Cr_{87.5}Al_{12.5} coating is lower than that of in the Cr₅₀Al₅₀ coating. XRD analysis also confirms the Fe reflection from the steel substrate in the Cr_{87.5}Al_{12.5} coating. In addition to Cr reflection from the coating and Fe reflection from steel substrate, in the Cr₁₀₀ coating, XRD characterization detects the major reflection of Cr₂O₃ and minor reflection of FeCr₂O₄. It is obvious that Cr is oxidized preferentially after heat treatment at 800°C for 2 h to form Cr₂O₃. Meanwhile, the formation of FeCr₂O₄ may occur according to the following reaction [13]:



During heat treatment, some amount of Cr₂O₃ reacts with Fe and oxygen to form FeCr₂O₄.

The cross-sectional BSE images of Al₁₀₀, Cr₅₀Al₅₀, Cr_{87.5}Al_{12.5} and Cr₁₀₀ coatings after heat treatment at 800°C for 2 h are shown in Figure 4. It can be seen in Figure 4(a) that the surface of substrate is rough and the Al coating becomes disappear. The EDX elemental maps show the local distribution of Al and O on the surface of steel substrate (Figure 5 (a)). This suggests that the uneven dark area on the steel surface is composed of Al-oxide. In addition, SEM-EDX elemental maps also indicate the presence of Al-rich area close to the steel surface. As the distance from the sample surface into substrate increases, the blue color intensity (Al distribution) tends to decrease and the magenta color intensity (Fe distribution) tends to increase, suggesting that the Al element is diffused inwardly

to the steel substrate. Some amount of Al reacts with Fe from the substrate to form FeAl as detected by XRD analysis, as shown in Figure 3(a).

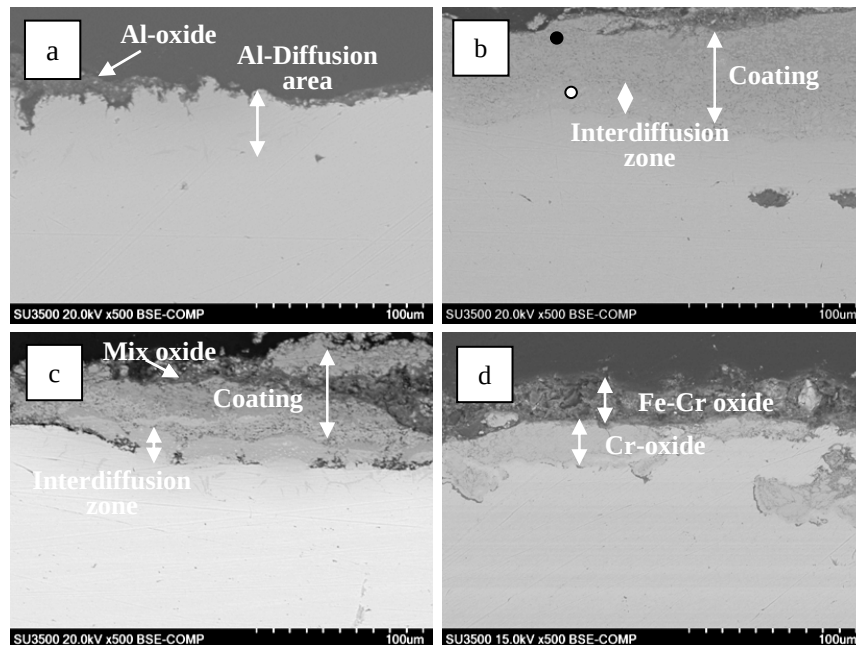


Figure 4. Cross-sectional BSE images of (a) Al_{100} , (b) $\text{Cr}_{50}\text{Al}_{50}$, (c) $\text{Cr}_{87.5}\text{Al}_{12.5}$ and (d) Cr_{100} coatings after heat treatment at 800°C for 2 h.

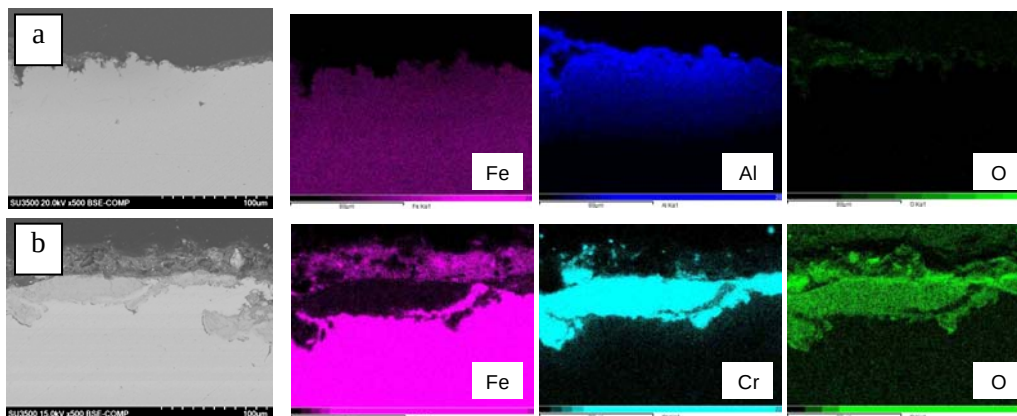


Figure 5. Cross-sectional BSE images and corresponding EDX elemental maps of (a) Al_{100} and (b) Cr_{100} coatings after heat treatment at 800°C for 2 h.

Meanwhile, a dense and more uniform coating structure are shown in the $\text{Cr}_{50}\text{Al}_{50}$ coating (Figure 4 (b)). The coating also exhibits strong adherence to the steel substrate. In this study, EDX point analysis was carried out in the coated sample. The results indicate that the coating composition near the coating surface (marked as black circle in Figure 4(b)) is composed of 51.52%at Al, 46.81%at Cr, 1.67%at Fe and coating/substrate interface (marked as white circle in Figure 4(b)) is composed of 34.44%at Al, 34.2%at Cr, 31.36%at Fe. It shows that from the coating surface to the coating/substrate interface, the Al and Cr concentration decrease and Fe concentration increases. The EDX results also reveal that an interdiffusion zone is formed at the coating/substrate interface. In the $\text{Cr}_{87.5}\text{Al}_{12.5}$ coating, localized mix oxides composed of 55.67%at O, 19.99%at Al, 11.99%at Cr and 12.35%at Fe

are formed in the coating. The interdiffusion zone is formed at the coating/substrate interface. The intermixing area between coating and oxide can also be seen from the cross-sectional image as shown in Figure 4(c). Meanwhile, in the Cr₁₀₀ coating (Figure 4(d)), the formation of Cr-oxide can be clearly seen from the result of EDX elemental maps as shown in Figure 5(b). Mostly Cr coating is oxidized to form Cr₂O₃ as detected by XRD analysis (see Figure 3 (d)). The formation of Cr-oxide after heat treatment could be related to the affinity of Cr for oxygen. Chromium has a very high affinity for oxygen, so it can be readily react with oxygen to form chromia [14]. Therefore, even if the partial oxygen pressure is low, the following reaction is likely to take place:



In addition, The EDX elemental maps also indicate the distribution Fe, Cr and O on the surface of Cr₂O₃ scale. This suggests that FeCr₂O₄ seems to be formed in the outer layer. The results as presented above indicate that the Cr₅₀Al₅₀ coating exhibits good adherence to the steel substrate and fine coating structure among the Cr₁₀₀, Cr_{87.5}Al_{12.5} and Al₁₀₀ coatings.

4. Summary

Four different compositions of Cr-Al coatings as Cr₁₀₀, Cr_{87.5}Al_{12.5}, Cr₅₀Al₅₀, and Al₁₀₀ have been prepared on low carbon steel by a mechanical alloying technique. The obtained results can be summarized as follow: the heat treatment of Cr-Al coatings on low carbon steel changes the coating structure. In the Al₁₀₀ coating, Al is preferentially diffused inwardly to steel substrate to form FeAl and Al-rich area near the sample surface. The Cr₅₀Al₅₀ coating shows a more uniform coating structure among Al₁₀₀, Cr_{87.5}Al_{12.5} and Cr₁₀₀ coatings. As Cr concentration increases, complex structures are formed in the Cr_{87.5}Al_{12.5} coating. For the Cr₁₀₀ coating, after heat treatment at 800°C for 2 h the Cr element is oxidized to form mainly Cr₂O₃.

Acknowledgments

The authors would like to thanks Research Center for Physics-Indonesian Institute of Sciences for financial support (Grant Number: 934/F/2014) of this project.

References

- [1] B Wang, J Wu, Y Zhang, Z Wu, Y Li, and W Xue 2015 *Surface & Coatings Technology* **269** 302
- [2] S PalDey, and S C Deevi 2003 *Materials Science and Engineering A* **355** 208
- [3] S Yang, F Wang, W Wu, and Y Niu 2001 *Oxidation of Metals* **56** 33
- [4] F A Varlese, M Tului, S Sabbadini, F Pellissero, M Sebastiani, and E Bemporad 2013 *Intermetallics* **37** 76
- [5] Y Zhang, X Peng, and F Wang 2004 *Materials Letters* **58** 1134
- [6] N Cinca, S Dosta, and J M Guilemany 2010 *Surface & Coatings Technology* **205** 967
- [7] B Song, S Dong, H Liao, and C Coddet 2015 *Surface & Coatings Technology* **268** 24
- [8] M Mohammadnezhad, M Shamanian, and M H Enayati 2012 *Applied Surface Science* **263** 730
- [9] M Mohammadnezhad, M Shamanian, M H Enayati, and M Salehi 2013 *Surface & Coatings Technology* **217** 64
- [10] A Canakci, F Erdemir, T Varol, and S Ozkaya 2013 *Powder Technology* **247** 24
- [11] S Romankov, W Sha, S D Kaloshkin, and K Kaevitser 2006 *Surface & Coatings Technology* **201** 3235
- [12] S Romankov, S D Kaloshkin, Y Hayasaka, Zh Sagdoldina, S V Komarov, N Hayashi, and E Kasai 2009 *Journal of Alloys and Compounds* **48** 386
- [13] X-X Luo, Z-J Yao, P-Z Zhang, Q Miao, W-P Liang, D-B Wei, and Y Chen 2014 *Applied Surface Science* **305** 259
- [14] J R Davis 1997 Elevated-Temperature Corrosion Properties of Superalloys in *ASM Specialty Handbook: Heat-Resistant Materials* (ASM International, Materials Park OH), p 146