Microstructure transformation of Cr-Al coating on carbon steel prepared by ball milling method as a function of tungsten doping

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Abstract. In present work, Cr-Al coatings containing 0, 1, 2, 3, and 5% W have been prepared on the surface of low carbon steel by 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. Afterward, the Cr-Al-W powder and substrate were mechanically alloyed in air for 1 hour. The heat treatment of coated samples was carried out at 800 °C in a vacuum furnace for 2 hour. In order to characterize the phase composition and microstructure of the coating before and after heat treatment, XRD and SEM-EDX were used. The analysis results reveal that the ball milling process induces the formation of homogeneous Cr-Al-W coating structure with a thickness of about 80 µm. The phase observation shows individual peaks of each starting elements, along with the occurrence of powder refinement and solid solution formation. After heat treatment, AlCr$_2$ and Al$_5$Cr$_3$ phases were formed. The addition of W accelerates the formation of AlCr$_2$, but inhibits the formation of Al$_5$Cr$_3$. The detail of the results was presented in this paper.

1. Introduction
Carbon steels have been widely used for wide range of applications due to its commercial consideration. However, it shows low oxidation resistance at high temperature [1]. In order to improve steel resistance against wear, oxidation, and corrosion at high temperatures, surface coatings can be applied on the surface of carbon steel. The Al-Cr coating is often used for corrosion resistance material due to its promising corrosion resistance to room temperature aqueous corrosion and hot corrosion of fused salt deposits [2,3].

In order to improve its properties, various studies based on Al-Cr coating have been conducted. The Al-Cr-Zr-N and Al-Cr-Co-Pe coatings were developed for corrosion resistance applications [4] and thermal barrier coating system [5], respectively. The composite ceramic coatings as (Al,Cr)$_3$O$_7$-Cr$_3$O$_4$ [6] and Al-Cr-N [7] were prepared to improve wear resistance. Currently, a mechanical alloying (MA) technique [8-12] has been used to deposit various coatings on the surface of materials. It was 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 the previous study, we successfully prepared Al-Cr coating by a mechanical alloying technique [12]. Currently, to improve the hardness of Al-Cr coating, the addition of tungsten (W) was conducted to the Al-Cr coating by a mechanical alloying technique. Heat treatment was also performed in order
to refine the coating structure. The metallographic characterizations of the coating before and after heat treatment were studied by means of XRD and SEM-EDX.

2. Experimental details

Commercial low carbon steel with an approximate dimension of 10x8x3 mm³ was used as substrate in this study. For coating deposition, the alloy surface was ground using SiC papers for up to 1200 grit. Prior to coating deposition, the specimen was ultrasonically cleaned in an aqueous solution and dried using hot flowing air.

The Cr₅₀-Al₅₀, Cr₄₉.₅-Al₄₉.₅-W, Cr₄₈.₅-Al₄₈.₅-W₃, Cr₄₇.₅-Al₄₇.₅-W₅ coatings were prepared using high purity Cr, Al, and W powders. Firstly, the coating powders were mixed in steel vial for 2 h using a shaker mill with powder to steel balls ratio of 1 to 10. The specimens were then subjected to mechanical alloying for 1 h.

The collisions of steel balls and powder on the surface of low carbon steel lead to deposition of coating powder on the steel surface. The heat treatment was carried out to improve the coating structure at 800 °C for 2 h in vacuum atmosphere of 5.6 Pa. The specimens were then allowed to cool down to room temperature in the same chamber. The phase compositions of the coating before and after heat treatment were analyzed by X-ray diffraction (SmartLab Rigaku) with Cu Kα radiation at 40 kV and 30 mA. The coating morphologies were characterized by means of scanning electron microscope equipped with energy dispersive X-ray spectrometer (SEM Hitachi SU 3500-EDX).

3. Results and discussion

The cross-sectional SE images of Cr₅₀-Al₅₀, Cr₄₉.₅-Al₄₉.₅-W, Cr₄₈.₅-Al₄₈.₅-W₃, and Cr₄₇.₅-Al₄₇.₅-W₅ coatings before heat treatment are shown in figures 1 respectively. It appears that the coatings were successfully deposited on the surface of low carbon steel and exhibits good adherence to the steel substrate. A relatively dense structure can be observed in the Cr₅₀-Al₅₀, Cr₄₉.₅-Al₄₉.₅-W, and Cr₄₈.₅-Al₄₈.₅-W₃ coatings. However, some micro cracks can be observed in the Cr₄₇.₅-Al₄₇.₅-W₅ coating. In addition, the cross-sectional images also show that the sample surface is rough.

Figure 1. Cross-sectional SE images of (a) Cr₅₀-Al₅₀, (b) Cr₄₉.₅-Al₄₉.₅-W, (c) Cr₄₈.₅-Al₄₈.₅-W₃, and (d) Cr₄₇.₅-Al₄₇.₅-W₅ coatings before heat treatment.

Figure 2 shows the X-ray diffraction patterns of Cr₅₀-Al₅₀, Cr₄₉.₅-Al₄₉.₅-W, Cr₄₈.₅-Al₄₈.₅-W₃, and Cr₄₇.₅-Al₄₇.₅-W₅ coatings before heat treatment. The XRD analysis shows reflections of Cr and Al in the Cr₅₀-Al₅₀ coatings as shown in figure 2a with no reflection peak of Fe from substrate of low carbon
steel. Meanwhile in the Cr_{49.5}-Al_{49.5}-W, Cr_{48.5}-Al_{48.5}-W_{3}, and Cr_{47.5}-Al_{47.5}-W_{3} coatings, Cr and W reflections can be clearly seen in Figures 2b, 2c, and 2d with relatively low diffraction peaks of Al.

![X-ray diffraction patterns](image)

**Figure 2.** X-ray diffraction patterns of (a) Cr_{50}-Al_{50}, (b) Cr_{49}-Al_{49}-W, (c) Cr_{48.5}-Al_{48.5}-W_{3} and (d) Cr_{47.5}-Al_{47.5}-W_{3} coatings before heat treatment.

The cross-sectional BSE microstructures and corresponding EDX elemental maps of Cr_{50}Al_{50} and Cr_{48.5}Al_{48.5}W_{3} coatings before heat treatment are shown in figures 3. In the coating layer, the coatings are composed of grey particles of Cr, dark area of Al, and white particles of W. The Cr-particles in the Cr_{48.5}Al_{48.5}W_{3} coating are smaller and more uniformly distributed compared to in the Cr_{50}Al_{50} coating. In the Cr_{48.5}Al_{48.5}W_{3} coating layer, as the distance from the substrate surface to coating surface increases, the particles become smaller and more uniform. Meanwhile, in the Cr_{50}Al_{50} coating, the Cr particles seem to be less smooth. The thickness of coatings, as shown in figure 3, is about 80 μm.

![Cross-sectional BSE microstructures](image)

**Figure 3.** Cross-sectional BSE microstructures and corresponding EDX elemental maps of (a) Cr_{50}Al_{50} and (b) Cr_{48.5}Al_{48.5}W_{3} coatings before heat treatment.

The XRD results in figure 2 show that although Al has the same concentration as Cr, the Al peaks appear significantly reduced than Cr peaks. This indicates that during milling, Al particles are more susceptible to deformation than Cr particles. In comparison to the results presented in figures 3a and
3b, it can be seen that the Al rich area is deformed to be the matrix surrounding the Cr rich area. As the W concentration increases, the Cr diffraction peak intensities tend to decrease. The peak intensity of W is relatively high despite the coating containing a small W concentration. This shows that the addition of W accelerates the smoothing and solid solution formation between Cr-Al. Al atoms are dissolved into Cr lattice to form Cr (Al) solid solution. This process is likely to occur due to hardness differences between Al, Cr, and W which hardness are about 160-350, 1060, and 3430-4600 MPa, respectively. The addition of harder materials accelerates the formation of a solid solution of a softer mixture. On the other hand, the addition of 5 at.% W (figure 1d) leads to crack formation in the coating, suggesting that the coating becomes more brittle with the increase of W concentration. When the coating surface is hit with the milling ball, the cracks can be generated easily.

The cross-sectional SE images of Cr50-Al50, Cr48.5-Al49.5-W, Cr48.5-Al48.5-W3, and Cr47.5-Al47.5-W5 coatings after heat treatment at 800 °C for 2 h are shown in figures 4. The Cr50-Al50, Cr49.5-Al49.5-W, and Cr48.5-Al48.5-W3 coatings exhibit good adherence to the steel substrate and a relatively dense structure can be observed. In the Cr47.5-Al47.5-W3 coating, however, some voids and micro cracks can be observed.

![Figure 4](image_url)

**Figure 4.** Optical cross-sectional images of (a) Cr50-Al50, (b) Cr49.5-Al49.5-W, (c) Cr48.5-Al48.5-W3 and (d) Cr47.5-Al47.5-W5 coatings after heat treatment.

The results of X-ray analysis of Cr50-Al50, Cr49.5-Al49.5-W, Cr48.5-Al48.5-W3, and Cr47.5-Al47.5-W5 coatings after heat treatment are shown in Figure 5. In Cr50-Al50, Cr49.5-Al49.5-W, and Cr48.5-Al48.5-W3 coatings, intermetallic phases as AlCr2 and Al5Cr3 are formed with AlCr2 as the main phase. Meanwhile, in the Cr49.5-Al49.5-W and Cr48.5-Al48.5-W coatings, Cr reflection can still be observed. The AlCr2 and W phases are observed in the Cr47.5-Al47.5-W5 coating. XRD characterization reveals that as W concentration in Cr-Al coating increases, the diffraction peak of AlCr3 increases and Al5Cr3 decreases. At 5 at.% W, however, the Al5Cr3 phase is not formed. This means that W addition inhibits Al5Cr3 phase formation.
Figure 5. X-ray diffraction patterns of (a) \( \text{Cr}_{50}\)-\( \text{Al}_{50} \), (b) \( \text{Cr}_{49}\)-\( \text{Al}_{49}\)-\( \text{W} \), (c) \( \text{Cr}_{48.5}\)-\( \text{Al}_{48.5}\)-\( \text{W}_3 \) and (d) \( \text{Cr}_{47.5}\)-\( \text{Al}_{47.5}\)-\( \text{W}_5 \) coatings after heat treatment.

The cross-sectional BSE images of \( \text{Cr}_{50}\)-\( \text{Al}_{50} \) and \( \text{Cr}_{48.5}\)-\( \text{Al}_{48.5}\)-\( \text{W}_3 \) coatings after heat treatment at 800 °C for 2h are shown in figure 6. As shown in figure 6a, the Cr-Al coating exhibits good adherence to the steel substrate and a dense structure can be observed. The results of EDX elemental maps show that Cr and Al are uniformly distributed in the coating. However, in the Cr-Al coating interface, the coating becomes Cr-rich and Al-depleted. On the contrary, some micro cracks are observed in the \( \text{Cr}_{48.5}\)-\( \text{Al}_{48.5}\)-\( \text{W}_3 \) coating (see figure 6b). Similar to the Cr-Al coating, Cr and Al are distributed in the \( \text{Cr}_{48.5}\)-\( \text{Al}_{48.5}\)-\( \text{W}_3 \) coating with small white precipitates detected by EDX as W-rich area.

Figure 6. Cross-sectional BSE images and corresponding EDX elemental maps of (a) \( \text{Cr}_{50}\)\( \text{Al}_{50} \) and (b) \( \text{Cr}_{48.5}\)\( \text{Al}_{48.5}\)\( \text{W}_3 \) coatings after heat treatment.
4. Conclusion
Four different compositions of Cr-Al coatings with the W addition as Cr$_{50}$-Al$_{50}$, Cr$_{49.5}$-Al$_{49.5}$-W, Cr$_{48.5}$-Al$_{48.5}$-W$_3$, and Cr$_{47.5}$-Al$_{47.5}$-W$_5$ have been prepared on low carbon steel by a mechanical alloying technique. The obtained results show a dense structure of Cr$_{50}$-Al$_{50}$, Cr$_{49.5}$-Al$_{49.5}$-W$_1$, Cr$_{48.5}$-Al$_{48.5}$-W$_3$ coatings. However, voids and microcracks are formed in the Cr$_{47.5}$-Al$_{47.5}$-W$_5$ coating. After heat treatment at 800 °C for 2h, the intermetallic phase of AlCr$_2$ and Al$_3$Cr$_3$ are formed in the Cr$_{50}$-Al$_{50}$, Cr$_{49.5}$-Al$_{49.5}$-W, Cr$_{48.5}$-Al$_{48.5}$-W$_3$ coatings. The high W concentration (Cr$_{47.5}$-Al$_{47.5}$-W$_5$) leads to suppression of Al$_3$Cr$_3$ formation.

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References
[1] Wang B, Wu J, Zhang Y, Wu Z, Li Y and Xue W 2015 Surf. Coat. Technol. 269 302
[2] Xu J, Chen Z Y, Tao J, Jiang S Y, Liu Z L and Xu Z 2009 Sci. China, Ser. E 52 1225
[3] Zhang M, Chen C, Zhang G, Rao Y and Ling G 2013 Physics Procedia 50 206
[4] Chen L, Liu Z Q, Xu Y X and Y Du 2015 Surf. Coat. Technol. 275 289
[5] Wolf W, Schulz R, Savoie S, Bolfarini C, Kiminami C S and Botta W J 2017 Surf. Coat. Technol. 319 241
[6] Dai X, Yan D, Yang Y, Chu Z, Chen X and Song J 2017 Ceram. Int. 43 6340
[7] Yang B, Chen L, Chang K K, Pan W, Peng Y B, Du Y and Liu Y 2012 Int. J. Refract. Metals Hard Mater. 35 235
[8] Mohammadnezhad M, Shamanian M and Enayati M H 2012 Appl. Surf. Sci. 263 730
[9] Mohammadnezhad M, Shamanian M and Enayati M H and Salehi M 2013 Surf. Coat. Technol. 217 64
[10] Canakci A, Erdemir F, Varol T and Ozkaya S 2013 Powder Technology 247 24
[11] Romankov S, Sha W, Kaloshkin S D and Kaevitser K 2006 Surf. Coat. Technol. 201 3235
[12] Hia A I J, Sudiro T, Aryanto D and Sebayang K 2016 J. Phys.: Conf. Ser. 739 012131