Influence of Heat Treatment on the Microstructure and Wear Properties of Arc-Sprayed FeCrAl/Al Coating

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Abstract: Intermetallic compounds formed during heat treatment of alloy coatings affect the coating structure and properties. In order to determine the phase changes and coating performance, FeCrAl (Fe Bal., Cr 26 wt.%, Al 6 wt.%) and Al (99.9 wt.%) coating was sprayed onto low carbon steel substrates and subsequently heat-treated at different temperatures. The effects of heat treatment on the microstructure, phase composition, tensile bonding strength, microhardness, and wear properties of the coatings were analyzed. The as-sprayed coating had a dense, layered structure with an average porosity of 3.6%. The microhardness of the as-sprayed coating was comprised of hard FeCrAl splats and ductile Al splats with an average microhardness value of 494 HV. At 300 °C, FeAl intermetallic compounds formed at the phase boundaries due to the diffusion of elements. The coating microhardness and wear resistance were affected by the uniform coating structure and the precipitation of FeAl intermetallic compounds. Compared with the annealed coatings, the as-sprayed coating had the lowest wear rate.

Keywords: arc spraying; FeCrAl/Al coating; heat treatment; FeAl intermetallics; hardness; wear resistance

1. Introduction

The arc spraying process is commonly used for protecting steel materials and remanufacturing worn parts so as to increase their service life. In comparison with other thermal spraying techniques, such as plasma spraying, arc spraying is preferred due to its high deposition efficiency, ease of operation, and relatively low cost of equipment [1–3]. Fe-based alloy materials such as FeCrAl possess suitable wear and corrosion properties in medium-to-high temperatures and also substitute NiAl bond coatings due to their good adhesion properties [4,5]. The high oxidation resistance of Fe-based coatings makes them good candidates for high heat elements in furnaces and boilers [3–5]. Iron aluminides are preferred to stainless steel and other superalloys because of the lower densities, lower costs, and availability of raw materials [6]. Al and Al alloys have been widely used in marine environments due to their outstanding corrosion resistance. In aggressive conditions, Al acts as a barrier coating by forming passive protective films that enhance the corrosion and high-temperature resistance [7]. Products formed after corrosion of the coating block the passages (pores and defects) for the electrolyte [8]. Due to the high strength-to-weight ratio, light Al and Al alloys are also applied in the automobile industry to replace heavy cast iron engine blocks [2]. FeCrAl applied by arc spraying has been used to improve the corrosion resistance of H13 steel hot dipped in aluminum [9]. Intermetallics and alloy coatings have been fabricated by arc spraying with the use of pre-alloyed or powder core wires. Simultaneously arc spraying two different pre-alloyed wires can develop pseudo-alloy coatings with better properties than the individual materials [10]. Pseudo-alloy coatings are hybrid coatings that combine the qualities of two different materials [11]. During deposition,
the materials are mechanically bonded but are not true alloys, hence the name pseudo-
allloys [12]. Several studies have been carried out to deposit pseudo-alloy coatings using
arc spraying processes such as 321 stainless steel/Al [10], Zn/Al [13], and Ti/Al [10,14].

Post-treatment techniques of alloys can further improve the coating properties. Heat
treatment affects the coating properties by significantly reducing cracks, pores, and re-
lieving residual stresses. Xu et al. [15] arc-sprayed Mg-Al composite coating and carried
out post-heat treatment on the coatings to obtain Mg-Al intermetallic compounds. The
microhardness and cohesion strength of the coating were significantly improved after heat
treatment. Chen et al. [16] showed that the heat treatment of Fe-Al composite coating
affected the oxide composition and the elemental diffusion of Fe-Al intermetallics. Zhou
et al. [17] found that intermetallic phases formed between the arc-sprayed Al coatings
and the P355NL1 steel substrate after annealing at different temperatures. The coating
microstructure became more compact at temperatures of 700 °C to 800 °C, which would
provide better bonding strength and corrosion resistance. Ekrem et al. [18] investigated
the wear properties of arc-sprayed Cu-Al intermetallic alloys. The wear resistance of
the alloys was affected by the intermetallic phases formed after heat treatment at 400 °C for
3 h. Most of the studies focused on the phase transformation of the alloy coatings after the
heat treatment. However, few studies reported the mechanical and tribological behavior of
pseudo-alloy coatings at different heat treatment temperatures.

This study aims to investigate the phase changes of Fe-based alloy during heat treat-
ment and the effects of intermetallic compounds on the coating performance. Given the
advantages of the pseudo-alloy coatings prepared by arc spraying, studying the microstruc-
ture changes during heat treatment and the wear behavior will provide an understanding
of the material degradation and characterization of the wear behavior of these coatings at
high temperatures for potential engineering applications. In our previous study [19], we
fabricated an arc-sprayed FeCrAl/Al composite coating, which exhibited good corrosion
properties at ambient temperature. In this work, FeCrAl/Al coatings were deposited on a
Q235 steel substrate, and subsequent heat treatment was performed at different tempera-
tures. The effects of heat treatment on the microstructure, phase structure, tensile bonding
strength, microhardness, and wear properties of the coatings were characterized.

2. Materials and Methods

2.1. Coating Preparation

Commercially available FeCrAl (Fe Bal., Cr 26 wt.%, Al 6 wt.%) and Al (99.9 wt.%)[8,20]
wires were arc-sprayed as the anode and cathode, respectively. The coating was deposited on
Q235 low carbon steel substrates (GB/T700) with a dimension of 50 mm × 30 mm × 8 mm.
The chemical composition of the substrate was: C (≤0.22); Si (≤0.35); Mn (≤1.4); P (≤0.045);
S (≤0.05); and Fe (Bal.). Before the spraying process, the substrates were ultrasonically
cleaned with acetone and then grit-blasted with 18 mesh steel grit to improve the adhesion
between the substrate and the coating. The spraying process was carried out using LSARC
arc spraying equipment (Shanghai Liangshi Co. Ltd., Shanghai, China). The arc spraying
parameters were as follows: voltage 44 V; current 200 A; air pressure 0.65 MPa; spraying
distance 150 mm. The effect of the spraying parameters was earlier studied [19] and the
orthogonal test analysis was used to obtain optimum parameters that give higher micro-
hardness, lower porosity, and lower wear rate. The coatings were annealed at temperatures
of 300, 400, 500, 600, and 700 °C in a box-type heat furnace (KF140) at a heating rate of
5 °C/min and the temperatures held for 4 h each before being cooled to room temperature
within the furnace. The heat treatment temperatures were set below and above the melting
point of Al (~660 °C) to explain the formation of FeAl intermetallic compounds. Previous
study by Kobayashi et al. [21] showed that the FeAl intermetallic layers in solid Fe and
solid Al grow and diffuse at a temperature range of 520–649 °C.
2.2. Microstructural Characterization

The morphology of the coatings was characterized by an FEI Quanta FEG 250 scanning electron microscope (SEM, Thermo Fisher Scientific, Waltham, MA, USA) equipped with energy dispersive spectroscopy (EDS, Bruker, Germany). The phase analysis of the coatings was identified with X-ray diffractometer (XRD, X’Pert Powder, PANalytical B.V., Almelo, The Netherlands) using Cu Kα radiation (λ = 1.5406 nm) operated at voltage 40 kV, current 40 mA, and scanning range 20–90°. The porosity of the coatings was calculated by ImageJ software (version 1.53p) using the grayscale method. Ten SEM images taken from different regions with a magnification of 1000× were used to calculate the average porosity. The microhardness was conducted with a Vickers indenter tester (Struers, Duramin-40, Ballerup, Copenhagen, Denmark) under a load of 100 gf and dwell time of 15 s. The microhardness was measured along the cross-section of the coatings and the average value obtained from ten measurements. The tensile bonding strength tests of the coatings were carried out in accordance with the ASTM C633-13 standard [22]. The tests were performed using a universal testing machine (DDL100; CIMACH, Changchun, China) at a tensile loading rate of 1 mm/min. The dimensions of the cylindrical samples were Ø25 mm × 50 mm. The tensile bonding strength was calculated by dividing the maximum tensile load by the cross-sectional area and the average determined by five tests for each sample, as shown in Equation (1).

\[
\text{Tensile bonding strength} = \frac{\text{Maximum tensile load}}{\text{Cross-sectional area}}
\]  

(1)

where cross-sectional area of the cylindrical sample is calculated by \( A = \pi r^2 \).

Sliding wear tests of the coatings were carried out according to the ASTM G133-05 standard [23] on a ball-on disk wear tester (CFT-1 wear testing machine, Zhongke Kaihua, Lanzhou, China). The counter body was a GCr15 ball with a diameter of 4 mm. When considering the nature of the coating and the sliding wear test equipment, the test parameters were chosen as follows: applied load of 4 N; sliding speed of 66.6 mms\(^{-1}\); oscillating stroke of 4 mm; and test duration of 30 min. The coefficient of friction was recorded automatically by the wear tester. The three-dimensional profiles of the wear track were measured by a laser confocal microscope (Olympus Corporation, LEXT OLS 4100, Tokyo, Japan). The wear test was conducted three times to ensure repeatability of the data, and the wear rates were calculated from Equation (2);

\[
W = \frac{V}{S \times P}
\]

(2)

where \( W \) is the specific wear rate (mm\(^3\)/N·m), \( V \) is the volume loss (mm\(^3\)), \( S \) is the sliding distance (80 m), and \( P \) is the normal load (N).

3. Results and Discussion
3.1. Coating Characterization

The as-sprayed coating (Figure 1a) consists of a typical layered structure with alternating FeCrAl and Al splats represented by light grey (region A) and dark grey (region B) areas, respectively [19]. The coating also comprises oxides and some pores. During the spraying process, molten droplets were oxidized as in-flight particles, as splash droplets on impact, and after deposition on the substrate [24]. The pores in the coating formed as a result of the partially melted particles and because air was trapped in the molten droplets during the solidification process [25].
Figure 1. SEM images in back scattered electron mode of the (a) as-sprayed coating and coatings annealed at (b) 300 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C, (f) 700 °C, respectively, composed of FeCrAl splats (region A), Al splats (region B), and intermetallic phase (region C).

The annealed coatings (Figure 1b–f) also show a similar layered structure with oxides, pores, and some cracks. At 300 °C and 400 °C, the coating morphology was similar to that of the as-sprayed coating. At 500 °C (Figure 1d), intermetallic phases (region C) formed between the interface of the FeCrAl and Al splats. The intermetallic phases (region C)—along the splat boundaries—increased with an increase in temperature (Figure 1d–f). At 500 °C and 600 °C, these intermetallic phases may have formed as a result of the elemental diffusion between the FeCrAl and Al splats in solid form. When temperatures reached 700 °C, which is above the melting point of Al (~660 °C), intermetallic phases formed through the diffusion of molten Al into the FeCrAl splats. However, some of the molten Al solidified and cooled, forming large solid droplets of Al2O3 oxides that initiated crack and pore formation along the interface boundaries. The size and number of pores affect the properties of the coatings [26]. The crack propagation could be attributed to the different
thermal expansion between the FeCrAl, Al, and intermetallic phases that generated tensile stresses during heating and solidification [27].

The EDS analysis (Table 1) of the coatings indicated that the light grey area (region A) was rich in Fe. The dark grey area (region B) was mainly Al, while the grey area (region C) comprised of FeAl intermetallic compounds that were also identified by the XRD analysis. At heat treatment temperatures of 500 °C to 700 °C, the distribution of the grey area (region C) increased and became more uniform while more Fe and Al dissolved in this interface.

| Coating  | Region | Fe (at. %) | Cr (at. %) | Al (at. %) | O (at. %) |
|----------|--------|------------|------------|------------|-----------|
| As-sprayed | A    | 71.13      | 12.57      | 11.64      | 4.66      |
|           | B    | 1.28       | 0.38       | 94.14      | 4.20      |
| 300 °C    | A    | 61.58      | 17.23      | 13.57      | 7.62      |
|           | B    | 0.65       | 0.18       | 96.77      | 2.40      |
| 400 °C    | A    | 61.34      | 12.90      | 20.66      | 5.10      |
|           | B    | 1.12       | 0.22       | 97.02      | 1.64      |
| 500 °C    | A    | 58.75      | 22.02      | 8.12       | 11.11     |
|           | B    | 1.31       | 0.29       | 95.00      | 3.40      |
|           | C    | 19.82      | 2.43       | 77.06      | 0.69      |
| 600 °C    | A    | 69.29      | 14.10      | 10.56      | 6.05      |
|           | B    | 2.31       | 0.32       | 91.61      | 5.75      |
|           | C    | 17.96      | 6.32       | 71.56      | 4.16      |
| 700 °C    | C    | 76.88      | 11.73      | 7.70       | 3.69      |
|           | B    | 24.20      | 4.32       | 56.90      | 14.57     |
|           | C    | 20.90      | 10.24      | 56.13      | 12.73     |

Table 2 shows the average porosities of the coatings. Figure 2 shows the grayscale images of the coating porosity obtained by ImageJ software. After adjusting the SEM images, the image with the most contrast and highest quality was selected for image analysis. The porosity was calculated by the given Equation (2) [25,26]:

\[ R = \frac{S_1}{S_2} \times 100\% \]  

where, \( R \) is the porosity of the coatings, \( S_1 \) is the total area of pores in one image view, and \( S_2 \) is the total area of the image view. The percentage porosity was repeated three times for each image to ensure accurate data, and ten images for each coating were analyzed.

The average porosity of the as-sprayed coating was 3.6%. After heat treatment at 300 and 400 °C, the porosity decreased slightly to 3% and 3.4%, respectively. Kang et al. [28] reported that structural relaxation of the coatings could affect the stability of the coating structure and atomic packing density to obtain a denser coating structure. The heat-treated coatings were densified to form a compact coating morphology. With a further increasing temperature, the porosity and cracks of the coatings increased. At 700 °C, the coatings had the highest porosity with cracks and pores distributed along the splat boundaries and around the oxide particles (Figure 1e,f).
3.2. Tensile Bonding Strength

The fractured surface images of the coatings are shown in Figure 3. The as-sprayed coating had a tensile bonding strength of 30 MPa. The bonding strength of the as-sprayed coating relates to the molten state of the particles during spraying. Unmelted particles, pores, and oxides in the coating reduce the adherence of the coating to the substrate. With regards to the ASTM C633-13 standard [22], the tensile bonding strength of the coatings relies on the adhesion between the coating–substrate interface and the cohesion strength between the coating. The fracture failure of the as-sprayed coating was an adhesive failure. With an increase in heat treatment temperature, the tensile bonding strength of the coatings decreased from 37.5 MPa to 20.2 MPa (Table 2). The coatings annealed at 300 and 400 °C also had an adhesive failure, which changed to cohesive failure in the coatings annealed at 500 to 700 °C.

The adhesive failure occurred at the interface of the coating and substrate. The coating annealed at 300 °C had the highest tensile bonding strength because of low porosity and dense coating microstructure after sintering during heat treatment. The coatings had a higher cohesion strength within the coating than the adhesion strength between the coating and substrate [29]. The cohesive failure occurred in the coatings annealed at 500 to 700 °C, showing that the adhesion between coating and substrate was greater than the cohesion strength within the coating. With increasing temperature, coating elements diffused and distributed to the substrate, thus improving the adhesion bonding strength at the coating–substrate interface. The propagation of cracks and pores along the splats interface and the coating oxidation reduced the cohesion strength. Vencl et al. [30] noted that pores and cracks within the coating act as fracture points that generate macroscopic failure resulting in cohesive failure.

To further examine the fracture mechanism of the coatings, SEM images of the fractured surfaces are presented in Figure 4. The fracture surface of the as-sprayed coating (Figure 4a) comprises cracks and pores. The unmelted particles formed during the spraying process reduced the mechanical interlocking of the coating–substrate interface. Thus, the incomplete contact regions and pores caused a brittle fracture of the coating. Zhou et al. [29] stated that pores and cracks could be attributed to the peeling off of unmelted particles from the substrate–coating interface. The fracture occurred at the coating–substrate interface, showing weaker adhesion strength.
Figure 3. Fracture topography of FeCrAl/Al coatings (a) as-sprayed, and coatings annealed at (b) 300 °C (c) 400 °C (d) 500 °C (e) 600 °C (f) 700 °C.

Figure 4. SEM micrographs in secondary electron (SE) mode of adhesive failure for (a) as-sprayed coating, (b) coating annealed at 300 °C, and (c) cohesive failure for coating annealed at 600 °C.

Regarding the coating annealed at 300 °C (Figure 4b), the coating comprised of flatter particles, fewer pores, and cracks that showed good wettability of the coating structure. The adhesion strength slightly improved because of the increase in temperature, which affected the sprayed particles along the interface. Komaki et al. [31,32] stated that the structure of particles and pores along the coating–substrate interface affect the adhesion strength. An increase in temperature improved the wettability of particles along the interface, thus improving the bonding of splat particles. The coating annealed at 600 °C (Figure 4c) fractured within the coating. The fracture is characterized by pores, cracks, and oxides that decreased the mechanical bonding of the splats within the coating [29]. Oxides formed along the boundaries of splat particles trigger cracks and lower the cohesion strength in the coating under tensile stress [33]. Thus, the oxides and pores in the coating acted as weak points leading to cohesive failure in the coating. Metallurgical bonding that occurred along the coating–substrate interface resulted in higher adhesion strength compared with the cohesive strength in the coating; thus, the brittle fracture occurred within the coating under tensile stress.
Table 2. Coating properties.

| Coating Temperature | Porosity (%) | Tensile Bonding Strength (MPa) | Type of Failure |
|---------------------|--------------|-------------------------------|----------------|
| As-sprayed          | 3.6          | 30.0                          | Adhesive failure |
| 300 °C              | 3.0          | 37.5                          | Adhesive failure |
| 400 °C              | 4.1          | 33.1                          | Adhesive failure |
| 500 °C              | 5.8          | 24.0                          | Cohesive failure |
| 600 °C              | 8.1          | 20.6                          | Cohesive failure |
| 700 °C              | 8.1          | 20.2                          | Cohesive failure |

3.3. XRD Analysis

The XRD pattern of the as-sprayed coating (Figure 5) shows that FeCr and Al were the main phases of the as-sprayed coating. Al₂O₃ and FeO oxides were also detected due to the atmospheric oxidation preference of Fe and Al elements during the spraying process. Previous studies stated that the formation of the dense Al₂O₃ hinders further oxidation of the underlying aluminum droplets [16,34]. In some cases, oxides in the coating contribute to the hardness, wear, and corrosion resistance of the coatings [24,35]. Lee et al. [2] found that FeO oxides formed during the spraying process acted as a solid lubricant that improved the wear resistance. However, high oxidation of the coatings during arc spraying forms oxide stringers along the intersplat boundaries that result in coating brittleness and poor intersplat cohesion [36]. The minor FeAl phases, as shown in our previous study [19], explained the possible reactions during spraying. The formation of FeAl phases may be in part due to the high-temperature interaction of FeCrAl and Al splats, forming a micro-metallurgical bonding.

![Figure 5. XRD patterns of the as-sprayed coating.](image)

The XRD patterns of the annealed coatings are shown in Figure 6. The main peaks of the coatings heat-treated at 300 and 400 °C were similar to those of the as-sprayed coating, consisting of FeCr and Al phases. A further increase in temperature at 500 °C caused phase
transformation as an intermetallic phase Fe$_2$Al$_5$ formed (shown by region C in Figure 1d), and only a small amount of Fe and Al reacted at this point [37]. Due to the slow cooling rate, the FeO oxidized to form Fe$_2$O$_3$ and Fe$_3$O$_4$ oxides. With an increase in temperature at 600 °C, Al phases reduced as the intermetallic phases Fe$_2$Al$_5$ increased (also shown by region C in Figure 1e). Since the heat treatment temperature was still below the melting point of Al (~660 °C), solid-state diffusion occurred between the Fe-rich phases and Al phases. Due to the high-temperature oxidation, the intensity of Fe$_2$O$_3$ and Fe$_3$O$_4$ oxides increased with a further increase in temperature. At 700 °C, the diffraction peaks of the Al phases were undetected while more FeAl intermetallic compounds formed, comprising of Fe$_2$Al$_5$, Fe$_3$Al, and FeAl (region C in Figure 1f), which is in agreement with a previous study by Zhou et al. [17]. From the XRD results, heat treatment of arc-sprayed FeCrAl/Al composite coating formed FeAl intermetallic compounds.

![Figure 6. XRD patterns of the coatings at different temperatures.](image-url)
3.4. Microhardness

Figure 7a shows the microhardness of the as-sprayed coating and substrate as a function of the distance from the coating–substrate interface. The microhardness of the substrate decreased from the coating–substrate interface due to the high impact of molten droplets during spraying that improved the coating–substrate adhesion. The as-sprayed FeCrAl/Al coating had an average microhardness of 494 HV$_{0.1}$, which was approximately 2.3 times that of the Q235 steel substrate. The hardness of the as-sprayed coating was comprised of alternating layers of hard FeCr and ductile Al phases [10].

![Figure 7a](image_url)

Figure 7. (a) Microhardness of the as-sprayed coating and substrate (b) average microhardness of the coatings.

Compared with the as-sprayed coating, the microhardness of the heat-treated coatings at 300 °C decreased to 437.8 HV$_{0.1}$, then later increased with an increase in temperature (Figure 7b). The decrease in coating microhardness at 300 °C was due to the change and reordering of the microstructure during annealing. Gialanella et al. described that [38] during heat treatment, the recovery and reordering of FeAl alloys powders occurred between 100–250 °C, whereas a complete reordering and recrystallization was noted at 700 °C. The fluctuation in the coating microhardness of the FeCrAl/Al coating explained the modification of the coating structure during the heat treatment [39]. The crystallization of the coating slightly increases both the hardness and toughness of the coating. At 600 °C, the higher microhardness could be attributed to the following: the FeCrAl and Al splats inter-diffused to form a more homogenous structure with intermetallic layers, and the precipitation hardening phenomenon of the Fe$_2$Al$_5$ intermetallic phases increased the overall microhardness [40]. By increasing the annealing temperature, the Fe and Al particles reacted, increasing the intensity of Fe$_2$Al$_5$ intermetallic compounds detected by the XRD. The microhardness of the coatings decreased at 700 °C and can be attributed to the deterioration of the coating structure with pores, oxides, and cracks initiated along the solidified Al phases and precipitation of Fe$_3$Al phases. Kobayashi et al. [21] investigated the hardness of the FeAl intermetallic compounds and obtained a hardness of HV320, HV660, and HV1000 for Fe$_3$Al, FeAl, and Fe$_2$Al$_5$ compounds, respectively. The microhardness of the coatings was dependent on various factors such as the composition distribution of the FeCr hard phase, the porosity of the coatings, and the presence of the intermetallic compounds and oxides [41].

3.5. Wear Behavior

To investigate the wear behavior of the as-sprayed and annealed coatings, the coefficient of friction (COF) and wear rate of the coatings were analyzed. The COF curves had
three distinct regions, as shown in Figure 8. The COF of the coatings increased rapidly during the first running-in stage (Region I), then slightly decreased during the transition period (Region II) between 100–400 s and achieved a steady-state (Region III) [42,43]. The running-in stage between 0–100 s was characterized by the rapid increase in the COF, attributed to the high frictional contact area between the GCr15 counter-body and the surface of the coatings [44]. During the steady-state period of the COF, the contact area increased as a result of flattened asperities, formation of the wear track, and oxide films on the worn surface [45]. In comparison with the annealed coatings, the as-sprayed coating displayed a lower COF, indicating good anti-friction properties.

Figure 8. COF of the coatings as a function of sliding time, which shows the running-in stage (Region I), transition period (Region II) and steady-state (Region III).

Figure 9 shows the 3D profiles of the wear tracks of the coatings. The as-sprayed coating had the smallest average wear track width compared with the annealed coatings. Among the annealed coatings, the coating at 700 °C had the least wear track width showing good wear properties.

Table 3 shows the wear rate of the coatings. In comparison with the annealed coatings, the as-sprayed coating had the lowest average wear rate of 24.03 × 10^{-6} mm^3/N·m. The higher wear resistance of the as-sprayed coating was due to the hard FeCr matrix that enhanced the load-bearing capacity and reduced the abrasion. According to Chen et al. [10], arc spraying Al with 321 stainless steel resulted in 321/Al composite coating with reduced oxide content, residual stresses, and microcracks compared with the 321 stainless coating. Thus, it can be suggested that adding Al to the FeCrAl during spraying improved the wear resistance of the composite coating because of the different properties of the two materials. The alternating layered structure between FeCrAl and Al mitigates crack propagation because of the inter-dispersed harder FeCrAl splats. FeCrAl particles acted as the load-bearing splats due to their higher hardness, while the Al particles improved the bond of the FeCrAl particles, thus slowing coating abrasion and enhancing the toughness, delamination, and shock resistance of the as-sprayed coating [10]. Additionally, the self-lubricating FeOoxides, detected by the XRD analysis, also improved the wear resistance of the coatings.
The average wear rate of the annealed coatings (Table 3) decreased with the increase in temperature, which is consistent with the coating microhardness. The coatings with higher hardness had a lower wear rate. In comparison with the as-sprayed coating, the higher wear rate of the annealed coatings at 500 °C to 700 °C can be attributed to the brittleness of the FeAl intermetallic compounds, which deteriorate the resistance to wear and coating deformation. Chen et al. [46] described that the brittle FeAl intermetallics decrease the wear resistance of the coating. During the reciprocating wear process, cracks propagated at the pores and caused a brittle fracture of the FeAl intermetallics in the coatings [47]. The wear resistance of the annealed coatings was mostly affected by the coating microhardness and the coating porosity. Despite the higher microhardness of coatings at 600 and 700 °C, the wear resistance of the coatings was lower than that of the as-sprayed coating due to the presence of larger pores and oxides that acted as crack propagation points [28].

At temperatures of 300 and 400 °C, the coatings had a higher wear rate due to their lower hardness. Additionally, during heat treatment, the coating asperities increased due to the coating roughness and the formation of Fe and Al oxidation films. At temperatures of 500 to 700 °C, the precipitation of the brittle Fe₂Al₅ and FeAl intermetallic phases in the coatings influenced the wear rate of the coatings. At 700 °C, the decrease in wear rate with increasing temperature can be attributed to the phase changes of Fe₂Al₅ to FeAl and Fe₃Al compounds. Also, the Fe₃O₄ oxides on the frictional behavior minimized the rapid removal of the coating layer due to the hardening effect, toughness, and better lubrication during wear [48]. These findings are consistent with previous studies [49]. Segu et al. [50]
explained that at lower annealing temperatures, fewer asperities carried the load, and the coating deformed easily. However, at higher temperatures, more asperities carried the same load, and due to the strength of the material and the reduced contact stresses on individual asperities, the wear was reduced. The porosity, oxides, and intermetallics phases of the coatings affected the wear resistance of the coatings [18]. The homogeneity of the FeCrAl and Al phases formed intermetallic compounds that increased the overall hardness of the annealed coatings. The FeAl intermetallic compounds and the hard Fe$_2$O$_3$ and Fe$_3$O$_4$ oxides, as shown by the XRD results, affected the wear properties. While the hardness of the coatings increased with temperature, the coating porosity also increased. Under the sliding wear conditions, the reciprocating motion of the counterpart material initiated micro-cracks in the pores and intersplat boundaries. The initiated microcracks increased during the reciprocating motion increasing the coating removal. The pores that formed along the solidified Al oxide particles affected the wear resistance of the coatings, which indicates that the wear resistance was related to the coating hardness, intermetallic compounds, and the microstructural characteristics of the coatings.

In order to understand the wear mechanism of the coatings, the worn surfaces of the coatings (Figure 10) were examined by SEM. The as-sprayed coating (Figure 10a) showed splat delamination caused by the oxides and microcracks along the plastic furrows. The furrows show a micro-cutting wear mechanism. Due to the alternating structure of FeCrAl and Al splats, the surface microcracks could not easily propagate to the underlying layers [49]. The oxidation on the worn surface may have resulted due to heat generated by friction during the relative sliding motion. Al in alternating structures of composite coatings was proven to have a higher resistance to crack propagation because of the lower energy release rate of the cracks. The wear mechanism of the as-sprayed coating was micro-cutting and splat delamination.

The worn morphology of coatings annealed at 300 and 400 °C (Figure 10b,c) shows a rough surface with furrows and wear debris that was deformed during the reciprocating motion of the counter body. Adhesive wear was the main wear mechanism. Brittle fracture of the splats occurred for coatings annealed at 500 to 700 °C (Figure 10d–f). Wear debris propagated from the furrows due to the brittleness of the intermetallic compounds. The annealed coatings fractured along the pores and cracks within the coating, breaking the splats during reciprocating motion. The abrasive wear debris was formed by spalling of oxides to form microcracks in the furrows. The oxides present in the worn surfaces of the annealed coatings formed during heat treatment and the sliding wear process. The oxides acted as a lubricant to reduce the wear loss of material [51]. The wear profile of the coating annealed at 700 °C shows a smoother surface with fewer furrows revealing less wear volume loss of the coating. The main wear mechanisms of the coatings annealed at 500 °C to 700 °C were abrasive wear and adhesive wear. Following the wear track volume and worn surface analysis, the as-sprayed coating had the lowest wear rate, which indicates a better wear resistance. Wear resistance of the heat-treated FeCrAl/Al coating increased with temperature.
Figure 10. SEM images (SE mode) of worn surfaces of (a) as-sprayed coating and coatings annealed at (b) 300 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C, (f) 700 °C, respectively.

4. Conclusions

FeCrAl/Al coatings were prepared in this study, and the effects of heat treatment on the microstructure, phase formation, tensile bonding strength, and wear behavior were investigated. Based on the experimental results, the following conclusions can be drawn:

1. FeCrAl/Al composite coating was prepared by arc spraying FeCrAl and Al wires as the anode and cathode, respectively. The coatings had a layered structure comprised of oxides, some pores, and alternating splats of FeCrAl and Al.

2. FeCr and Al were the main phases of the as-sprayed coating. The FeAl intermetallic phases (Fe$_2$Al$_5$, Fe$_3$Al, FeAl) were formed at 500 °C and increased with increasing heat treatment temperatures from 500 to 700 °C.

3. The as-sprayed coating had a microhardness of 494.01 HV$_{0.1}$, which was 2.3 times that of the substrate, while the microhardness of the annealed coatings slightly increased with increasing heat treatment temperature. The hardness of the heat-treated coatings was influenced by the precipitation hardening effect of the iron oxides (Fe$_2$O$_3$ and Fe$_3$O$_4$) and the FeAl intermetallic compounds.

4. The average wear rates of annealed coatings decreased with increasing temperature. The as-sprayed coating possessed the highest wear resistance compared with the annealed coatings. The formation of the hard and brittle FeAl intermetallic phases, coating microhardness, and microstructure influenced the wear resistance of the annealed coatings.

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