Surface Hardening of Medium Carbon Steels by Aluminization

By J.K. CHEN
S.M. CHAN

Synopsis:
Solid state surface aluminization of a medium carbon steel for roll applications is investigated. The processing temperatures range between 500°C and 700°C, and the diffusion time varies from 2 to 6 hours. The structures, phases, and mechanical properties of the coating layers are studied. The thickness of the coating layers are formed in the range of 20~90um. The activation energy for growth of coating layer is approximately 30.1 KJ/mole. The coating layer consists of two major phases. The Fe2Al5 phase is formed on the surface, while a solid solution with Fe3Al structure is formed at the interface between surface Fe2Al5 layer and the substrate. The coating’s hardness is as high as Hv826 while keeping the substrate hardness at relatively high level.

Keywords: Diffusion, Aluminization, Surface hardening, Fe-Al intermetallic compounds

1. Introduction

Medium carbon alloy steels with adequate hardenability and mechanical properties are often used for various roll applications [1]. There are many ways to improve their service lives by increasing the surface hardness of these cast steel rolls. Rapid heating processes using induction heating [2], plasma [3], or electron beam treatment [4] are widely used to modify the microstructures on roll surfaces. On the other hand, hard surface coatings are often applied. Typical hard coatings on roll surface include processes such as chromium plating [5] and thermal spraying [6-7]. Other than improved hardness, the hard coatings can provide advantages including improved corrosion resistance, fatigue, and even high temperature stability for varied functionality.

The Fe-Al intermetallics are renowned for their chemical and high temperature stability. They can be used as surface coating on steels by hot dipping processes [8]. In hot dipping processes, the materials are first dipped in molten aluminum bath and are then subject to high temperature reaction diffusion at 700-1000°C to form surface Fe-Al intermetallics. Such formed surface Fe-Al intermetallic coating can withstand temperatures up to 1093°C (2000°F) [9]. However, the disadvantage of hot dipping process is apparent. The high temperature diffusion process can cause the strength of substrate material to drop significantly.

Other routes, such as pack cementation, were also developed to form surface layers of Fe-Al intermetallics. The pack cementation process utilized halides as activators to activate the aluminization reaction on substrate surface. The halides undergo gas decomposition to protect the materials from oxidation and aid aluminum powders to react with Fe and form Fe-Al intermetallics [10]. The treatment can be performed at wide range of temperatures via mechanisms of gas phase reactions [11,12].

The current study explores the possibility of using Fe-Al intermetallics as a surface coating on a Ni-Cr-Mo containing medium carbon steel for roll applications. The aim is to reduce the treatment temperature to lower than 700°C, so the reduction of matrix strength can be controlled. The kinetics and microstructures of thus formed coatings are discussed.

2. Experiments

The medium carbon Ni-Cr-Mo containing alloy steel with composition of 0.53wt%C, 0.5wt%Si, 0.6wt%Mn, 1.5wt%Ni, 1.05wt%Cr, and 0.4wt%Mo was used as the substrate. The substrate material was made by centrifugal casting with a hardness of Hv243.

The substrate material was first cut into 10x10x5mm pieces and ground using #200 grid sandpapers before being ultrasonically cleaned in acetone for 10 minutes. The activator employed in this study was AlCl3 powders. These were mixed...
with 50-100μm pure Al and Al2O3 powders to constitute the compaction agents. The proportions of compaction mixtures were 2wt%Al + 4 wt%AlCl3 + 94wt% Al2O3.

The cleaned specimens were buried in compaction mixtures for isothermal treatment at different temperatures and for varied treatment time. The treatment temperatures were selected to include 500, 550, 600, 650, and 700°C. And the treatment time were controlled to include 2, 4, 6, and 12 hrs before cooling down to room temperature in furnace.

The coated specimens were observed using both optical microscope and SEM (scanning electron microscopy) to analyze the cross section micro-structures and thickness of the surface coatings. EDS (energy dispersive spectroscopy) and XRD (X-ray diffraction) using Cu Kα radiation were also made to determine the compositions and phases that were present on the specimen surfaces. Vickers microhardness tests using 25g force were performed on cross sections of the hard coatings to measure their hardness.

3. Results and Discussion

3.1 Effects of Temperature on Surface Micro-structures

![Figure 1: SEM structures of surface coatings treated at (a) 600°C, (b) 650°C, and (c) 700°C for 6 hrs.]

Figure 1 shows the effects of temperature variations on surface coating structures with the treatment time fixed at 6hrs. The thickness increases from 53μm 82μm with treatment temperature increased from 600°C to 700°C. When treatment temperature increases over 650°C or approaches melting point of aluminum, large amount of porosity is observed in the coatings (Fig. 1(b) and 1(c)). Both the coating thickness and porosity increases with treatment temperatures.

The SEM observations (Fig.2) on the specimens treated at 700°C for 2 hours indicate that the coatings consist of two layers. The Al concentration in the outer layer is found to maintain at a relatively constant level in consistent with approximately Fe5Al3 composition. The Al concentration drops gradually in the inner layer with increasing distance from the surface. This is due to that there is a large solid solution region in the Fe-Al phase diagram ranging from ~0 to 30 wt%Al. With these in mind, it is reasonable to have higher Al concentration in the outer layer since there is higher aluminum potential at the surface, while Al concentration drops when aluminum diffuses toward the substrate.

![Figure 2: EDS analysis of surface coating layers (700°C, 2hr): (A) Fe5Al3 and (B) Fe3Al.]

The XRD analysis results as shown in Figure 3 support the above observations. There are mainly two types of Fe-Al intermetallic phases present in the XRD analyses, Fe5Al3 and Fe3Al. The intensity of Fe5Al3 increases with temperature and appears to be much stronger than the intensity of Fe3Al.

The Fe3Al phase is a solid solution of Fe and Al and has DO3 crystal structure [13] which is similar to that of bcc Fe [14]. Since Fe3Al is richer in Fe, this layer grows from the substrate side toward the Al powder compaction. The existence of Fe3Al phase with wide range of aluminum concentration benefits the adherence of surface Fe5Al3 coating with the substrate. Although Fe3Al has similar crystal structure as the substrate, the XRD results show that the Fe3Al phase lessens at lower temperatures (Fig.3). This implies that the pack aluminization process has ample supply of Al to the surface of steel substrate to make Al rich Fe5Al3 phase more dominant in the coatings. The thinner Fe3Al layer as shown in Figure 1 is consistent with such observation.

![Figure 3: XRD spectra of surface coatings at varied temperature while treatment time is fixed at 6hr.]

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3.2 Effects of Treatment Time on Surface Microstructures

Figure 4 shows the SEM microstructures of specimens treated all at 700°C for different durations. The total thickness of surface coating layers increase with treatment time. From these micrographs, it is noted that although the total coating thickness increases, the thickness of Fe$_3$Al diffusion layer appears to decrease from 14µm to lower than 5µm with increasing treatment time.

At 700°C, Fe$_3$Al first form on the substrate surface, while the Fe$_2$Al$_5$ starts growing from outside where higher Al potential is present. The dissolution of Fe$_3$Al by Fe$_2$Al$_5$ growth with increasing time implies that there is more aluminum diffusing toward the substrate than iron diffusing outward. It is this effect that causes Fe$_3$Al layer to disappear and the higher Al-containing Fe$_2$Al$_5$ keeps growing. Such effects can also cause the Fe$_3$Al layer growth to be suppressed with decreasing temperatures when Fe diffusion is further reduced.

The difference in Fe and Al diffusion rate gives rise to Kirkendall effect and causes the inter-phase boundary to migrate. Furthermore, porosity forms due to Kirkendall effect. It is clear in Figures 4 and 1 that the coatings consist of porosity especially in the coatings treated at temperature higher than 600°C. On the other hand, the porosity appears to reduce with decreasing temperature and time (see for example, Figure 1(a) and Figure 4(a)) indicating that the Fe and Al inter-diffusion is more restricted under these conditions.

Since the total Al concentration in the compact is fixed, the porosity gradually move outward to the surface of coatings when treatment time further lengthens and surface Al potential starts to flatten out due to completion of surface reaction. In the specimen treated at 700°C for 6hrs (Figure 4(c)), the porosity apparently locates closer to the surface of the coatings.

Figure 5 shows the effects of treatment time on the XRD of 650°C treated specimens. It is clear that both the Fe$_3$Al and Fe$_2$Al$_5$ intensity is fairly small for 0.5hr treated specimen. The Fe$_2$Al$_5$ peaks become more prominent than those of Fe$_3$Al when treatment time is increased. This is consistent with the SEM observations that the amount of Fe$_2$Al$_5$ increases with time while the thickness of Fe$_3$Al is reduced.

3.3 Kinetic Evaluations of Fe-Al Coatings

In the current study, the main Fe-Al intermetallic compound formed in the coatings is Fe$_2$Al$_5$. The Fe$_2$Al$_5$ phase becomes the dominant phase for treatment temperatures lower than 700°C, therefore the discussions on kinetics of coating growth are emphasized on this layer. The thickness of coating formed by diffusion is expressed as:

\[ h = k_e \exp \left( \frac{-E_A}{2RT} \right) t^n \]

Where \( h \) is the thickness of coatings, \( k_e \) is constant, \( R \) is gas constant, \( T \) is treatment temperature in °K, \( t \) stands for treatment time (sec), and \( E_A \) represents the activation energy (J/mole) for effective Al diffusion to form Fe$_2$Al$_5$. The activation energy, \( E_A \), can thus be obtained by plotting ln(\( h \)) vs. 1/T (Figure 6).

Figure 6: Plot of natural logarithm of coating thickness (um) with reciprocal of T (°K) for kinetic evaluations.
The slope in Fig. 6 is equal to $-\frac{E_A}{2RT}$ and thus $E_A$ is evaluated to be 30.1 kJ/mole. It is noted that such activation energy is even lower than that of carbon in steels and that reported by other literatures [10, 15]. This means that the Fe$_2$Al$_5$ layer is formed at relatively high growth rate. The low activation energy is consistent with the fact that pack aluminization involves phase reaction in forming Fe-Al intermetallics [12].

3.4 Hardness of Surface Coatings

The main purpose of current study is to increase the surface hardness while keeping the softening of matrix as low as possible. Therefore, it is important to monitor the effects of aluminization treatment temperatures upon both the matrix and surface coating layers. Figure 7 demonstrates a series of samples tested using Vickers microhardness indentations.

![Figure 7: Optical micrographs of microhardness indentations on matrix and surface coatings treated with different temperatures and durations: (a) 500°C 12hrs, (b) 550°C 6hrs, (c) 600°C 6hrs, (d) 650°C 6hrs, and (e) 700°C 6hrs.](image)

It is observed that the indentation size in the substrate increases with increasing temperature. While in the surface coating layers, the 600°C and 650°C appear to bear the smallest indentation sizes. It means that the highest hardness is obtained at intermediate temperature range of 600-650°C.

Figure 8 shows the variation of microhardness with treatment temperatures. The microhardness of surface coatings adversely increases with treatment temperature from 500°C till 600°C. The highest hardness of Hv826 is obtained in specimens treated at 600°C and then drops with increasing treatment temperature. The drop of hardness in higher than 600°C treated coatings can be explained by pronounced porosity in coatings as shown in Figures 1 and 4.

![Figure 8: Variation of microhardness with treatment temperatures (all treated for 6hr except the untreated substrate for comparison purpose and the 500°C specimen treated for 12hr.)](image)

It is also observed in Figure 7 that while the matrix is lightly etched using 2% Nital, the surface Fe-Al intermetallic coating is relatively intact indicating its improved corrosion resistance over the substrate material. When treatment temperature decreases to lower than 600°C (Figure 7(a)-(b)), the surface coating structures appear to become less corrosion resistant. It is reasonable to suspect that coatings formed at these temperatures are lower in aluminum concentration and thus affect the corrosion properties of surface coating.

Since the concentration of coating layer is somewhat differentiating from the stable Fe$_2$Al$_5$ intermetallic composition, the formed intermetallic compound phase can thus bear slightly lower hardness. The coatings formed at lower temperature (<600°C) therefore demonstrate a slight hardness drop as shown in Figure 8.

Figure 8 also shows that the substrate hardness maintains at relatively high level for specimens treated at temperatures lower than 550°C in comparison with untreated substrate material. The microhardness of substrate demonstrates a greater drop from Hv243 to below Hv165 due to the growth of ferrite structures when treatment temperatures are increased over 550°C.

4. Conclusion

The current study successfully forms Fe-Al intermetallic layers on the surface of a Ni-Cr-Mo containing medium carbon alloy steel by pack aluminization process. The total thickness of Fe$_2$Al$_5$ and Fe$_3$Al layers ranges between 20–90μm using 500–700°C low temperature treatments. The etched microstructures show that these coatings are more corrosion resistant than the matrix. Formation of
Fe₃Al as an intermediated layer between the substrate and surface Fe₃Al₅ layer is believed to benefit the adherence of surface coating.

The Al-rich Fe₃Al₅ grown inward from the outer Al powder compaction competes with the Fe-rich Fe₃Al layer grown outward from the steel substrate. Fe₃Al₅ eventually dominate the compositions of the coating layers due to higher diffusion rate of Al in Fe than Fe in Al atoms. This is observed in specimens treated at lower temperatures or prolonged treatment time.

The coatings demonstrate the highest hardness of Hv826 by 600 °C treatments. When the treatment temperature is further increased to exceed the melting point of aluminum, porosity is increased due to Kirkendall effects and hardness drops in the coatings. On the other hand, diffusion becomes limited with lowering temperatures. The lower Al diffusion causes the coating composition to deviate slightly from the stable Fe₃Al₅ composition. Therefore, both the coating hardness and corrosion resistance drops with decreasing treatment temperatures under 600 °C.

The activation energy of Fe₃Al₅ growth kinetics is estimated to be 30.1 kJ/mole. This value is lower than that needed for interstitial diffusion in steels. It confirms that the Fe-Al coating formation is based upon gas phase type of reaction mechanisms.

5. REFERENCES

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