

Pack Diffusion Aluminizing of Carbon Steel

M.E. Abd EL-AZIM, K.E. MOHAMED, H.M. SOLIMAN and F.H. HAMMAD-Dept. of Metallurgy-Nuclear Research Center - Atomic Energy Authority - Cairo Egypt

Abstract

The pack cementation process is ideally suited for the formation of well bonded diffusion aluminide coatings. A study has been made on the aluminizing of low carbon steel in halide activated pure Al and Fe-Al packs. The effect of Al content in the pack, temperature and time of aluminizing as well as halide type and content on the structure and thickness of the aluminide layer has been investigated. The results were evaluated by metallography, X-ray diffraction and energy dispersive X-ray analysis.

Riassunto

Il processo di cementazione a polvere è l'ideale per la formazione di rivestimenti ad ottima aderenza a base di alluminuri ottenuti per diffusione. È stata studiata l'alluminizzazione di acciaio a basso carbonio con polveri di Al puro e leghe Fe-Al attivate con alogenuri. L'effetto del tenore di Al nella polvere della temperatura e del tempo di trattamento così come il tipo e la percentuale di alogenuro sulla struttura e sullo spessore del ricoprimento è l'oggetto della ricerca. I risultati sono stati determinati per via metallografica, con diffrazione ai raggi X e con l'analisi di raggi X a dispersione di energia.

Introduction

Protective coatings are formed on structural materials used in aggressive environments to decrease the surface degradation that occurs upon exposure to high temperatures and corrosive atmospheres. Aluminide coatings on steel increase its corrosion resistance in hydrocarbon and sulphurous atmospheres [1] and enhance its oxidation resistance [2,3]. The pack diffusion aluminized steels are used widely in parts as conveyor chains, retorts, thermocouple sheaths, frames of heat treatment furnaces, baffle plates, steam engine exhausts, oil refinery equipment and heat exchanger components in coal gasification and liquification applications [1-3]. The kinetics of the pack diffusion aluminizing process is controlled by various parameters which affect the microstructure, thickness and, consequently, the protective properties of the aluminide coating layer. These parameters include time and temperature of treatment, aluminium content and nature of the pack cementation powder mixture, type and content of halide activator and finally the substrate material.

A number of investigations have been done on the microstructure and phase composition of pack diffusion aluminide coatings on plain carbon steel [1-5]. However, different phase analysis results were reported by different authors depending on the conditions of a particular diffusion treatment.

The aim of the present research is to study the role of some metallurgical factors, which affect the kinetics of formation of aluminide coating on plain carbon steel ($\Delta 37$ with 0,22% C) produced by Delta Steel Mill Company, Egypt, to be recommended for some national industries. The study also includes the microstructure, chemical composition and phase analysis of these layers.

Experimental Procedures

Pack diffusion aluminizing was conducted on carbon steel disc samples of 14-22 mm diameter with 2-3 mm thickness machined from as received hot rolled bars. The specimens were polished, degreased, washed and dried before aluminizing.

The steel specimens were packed with powder mixture containing Al source, halide activator and calcined alumina to prevent fusion and coalescence of Al powder. Two types of Al source powders were investigated. The first was pure Al powder. The second was Fe-Al powder mixture containing different amounts of Al. This powder mixture was sintered at 850°C for 3 hours before use. The particle size of the powder was smaller than 500 μm . The process was performed in austenitic stainless steel container sealed with a paste of

kaoline and liquid sodium silicate. A wide temperature range of aluminizing from 700-950°C was investigated with exposure time up to 19 hours.

Metallographic investigation was carried out to evaluate the thickness and microstructure of the aluminide coating. In addition, X-ray diffraction and energy dispersive X-ray analysis were performed to determine the phase composition and the Al-concentration profiles.

Results

Aluminizing Using Pure Al and Fe-Al Packs

Pack aluminizing of low carbon $\Delta 37$ steel was carried out at 900°C for 4 hours using pure Al pack having 5 wt.% Al and in Fe-Al pack consisting of 99% [70%(70% Fe+30% Al)+30% Al_2O_3]+1% NH_4Cl by weight at 900°C for 19 hours. Aluminizing in pure Al pack led to strong adherence of the powder particles to the surface of the coated samples, while Fe-Al pack led to the formation of aluminide coating with smooth surface.

Moreover, X-ray diffraction results revealed that aluminizing in pure Al pack is accompanied by the formation of the Al-rich phases FeAl_3 and Fe_2Al_5 while Fe-Al pack led to the formation of Fe_3Al and FeAl phases in the aluminide layer (Fig. 1).

Further investigations were carried out in aluminizing medium on the base of Fe-Al powder mixture as Al source.

Effect of the Pack Diffusion Parameters on the Formation of Aluminide Layers

Aluminium activity in the pack mixture

Aluminizing of low carbon steel having 0.22 wt.% carbon was carried out at 850°C for 4 hours in pack mixture consisting of 99% [70% (Fe + Al) + 30% Al_2O_3] + 1% NH_4Cl by weight, with Al content in Fe-Al mixture changing from 20 to 70%.

Increasing the Al content in the pack mixture led to noticeable increase in the thickness of the aluminide layer. Example microstructure is given in Fig. 2. The data given in Table 1 clearly indicate remarkable thickness increase upon increasing the Al content in the Fe-Al from 20 to 30% and also from 60 to 70%.

As shown in Fig. 2, the aluminide coating consists of columnar grains of α solid solution of Al in Fe as an inner layer and Fe_3Al and FeAl intermetallic phases as an outer layer. As the Al content in the Fe-Al increases from 20 to 50 wt. %, the thickness of the outer layer of the coating increases from few microns to about 30 microns.

The aluminium concentration profiles obtained by the energy dispersive X-ray analysis for aluminide layers formed at 850 and 900°C for 4 hours in pack mixtures containing 30 and 50% Al in Fe-Al are shown in Fig. 3. The corresponding surface concentration of Al increases from 15 to 25 wt.%. The high Al surface concentration is maintained constant to a depth of 20 μm for samples treated in high Al content pack of 50% at 850°C for 4 hours. Gradual decrease of the Al concentration was observed with the depth of the aluminide

layers obtained at 850° and 900° C for the pack mixture containing 30% Al in Fe-Al.

TABLE 1 - Effect of Al content in the Fe-Al of the pack mixture on the aluminide coating layer thickness.

Composition of the Fe-Al Component (wt. %)		Average Coating by Thickness (μm)
Al	Fe	
20	80	37
30	70	62
40	60	68
50	50	72
60	40	88
70	30	160

It is important to note that the diffusion zone and the aluminium concentration at equal distances in the aluminide layers obtained from mixtures of the same Al content are increased upon increasing the treatment temperature from 850° to 900°C. Similar behaviour was also observed upon increasing the aluminizing time from 4 to 8 hours at 850°C.

Fig. 3 reveals that the thickness of the outer layers of the aluminide coatings in which the Al concentration is ≥ 15 wt.% where the intermetallic compounds Fe_3Al and FeAl may represent the major phases are about 7 and 30 μm for Al contents of 30 and 50% in the Fe-Al mixture, respectively. This is consistent with the thickness measurements from microstructural analysis (Figs. 2 and 4).

Effect of temperature and time

The pack diffusion aluminizing was investigated in the temperature range 700-950°C for time intervals up to 19 hours in a powder mixture consisting of 99% [70% (70% Fe + 30% Al) + 30% Al_2O_3] + 1 % NH_4Cl . It was found that the thickness of the aluminide layer increased with increasing the aluminizing temperature as shown in Fig. 4.

The relation $\log x^2$ versus $1/T$ at constant aluminizing time of 4 hours was found to be, to a good approximation, linear as shown in Fig. 5 and the results can be expressed by the following equation:

$$x^2 = K_0 t \exp \left(\frac{-Q}{RT} \right) \quad (1)$$

where

x = coating layer thickness

t = aluminizing time

T = aluminizing temperature (K)

K_0 = constant

R = universal gas constant

Q = activation energy of diffusion.

Regression analysis gave activation energy of 57.8 K cal/mole.

The results of Fig. 6 indicate that a parabolic relation exists between the thickness of the aluminide layer formed at 850° or 900° C and the coating time.

Effect of activator

Three different halide activators NH_4Cl , NaCl and AlF_3 were tried. A powder mixture of 99% [70% (70% Fe + 30% Al) + 30% Al_2O_3] + 1% activator was used to aluminize $\Delta 37$ specimens at 900°C for 4 hours. The aluminide layer thickness obtained with different activators was 64 μm ; 103 μm and 111 μm for NaCl , NH_4Cl and AlF_3 , respectively.

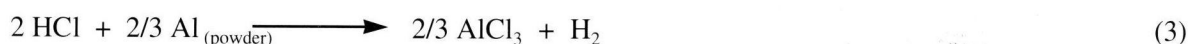
Increasing the NH_4Cl content from 1 to 6%, with the other coating parameters remaining unchanged, led to slight increase in the coating thickness as shown in Table 2. A slight decrease was noted with further increase of activator content up to 12%.

TABLE 2 - Effect of NH_4Cl concentration in the pack mixture on the aluminide layer thickness.

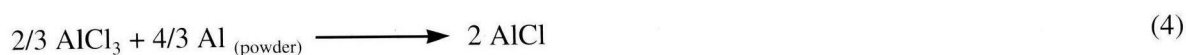
Concentration of NH_4Cl (wt. %)	Average Coating Thickness (μm)
1	102
3	113
6	124
9	110
12	104

Discussion

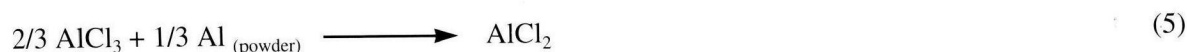
Pack aluminizing is a diffusion process involving various steps. During the heating period, the following reactions take place in the aluminizing pack mixture;



At high temperatures (> 700°C) aluminium subchlorides are formed by the reactions;



and



Thermodynamic calculations, however, showed that AlCl_2 is dominating at temperatures $< 1000^\circ\text{C}$ [6]. At the present investigation the process temperature range is $\leq 950^\circ\text{C}$, thus further aluminizing is accomplished either by the reaction between aluminium subchloride AlCl_2 and the steel substrate with the formation of intermetallic phases (eqs. 5 and 6) or by self-reduction of AlCl_2 with the separation of active aluminium atoms at the surface of steel substrate and its subsequent diffusion (eq.7). It should be mentioned that the formation of higher Al phases FeAl , FeAl_2 , Fe_2Al_5 or FeAl_3 is also possible by equations similar to eq. 6, depending on the different process parameters.



Two hypothesis have been put forward to explain the mechanism of formation of diffusion layers in its initial stages when intermetallic phases are formed on the surface of the treated material [6]. According to the first one, the diffusing element is accumulated in the surface layer to the solubility limit, then intermetallic phases are formed. The second hypothesis assumes the formation of intermetallic phases in the first moments on the substrate surface. Further growth of the diffusion layer is accomplished through inter-diffusion of saturating and base elements.

The process parameters in the present investigation led to the formation of the intermetallic phases Fe_3Al and FeAl . The presence of Fe in the pack mixture reduces the activity of Al in the pack and prevents the formation of the brittle phases Fe_2Al_5 and FeAl_3 . Similar results have been reported [2-4].

The formation of FeAl_3 in addition to FeAl , Fe_3Al and α -solid solution as a result of aluminizing in pure Al pack containing 10 wt. % Al is also consistent with previous findings [2] obtained for 0.3% C-steel aluminized at 900°C in pure Al pack containing 5 wt.% Al. This particular structure obtained in the pure Al pack mixture is explained, most probably, by the occurrence of Al diffusion from the liquid phase in the points of contact between the Al particles and the surface of the coated article in addition to the main diffusion process from the gaseous phase. The activation energy of 57.8 k. cal/mole obtained for low C-steel aluminized in the temperature range 700°C - 950°C is in good agreement with previous aluminizing results [3] and also with the activation energy for diffusion of Al in Fe-Al alloys [5]. This can lead to the suggestion that Al diffusion in the substrate is the rate controlling step in the pack aluminizing process of low C-steel.

The effect of different halide activators on the kinetics of the aluminizing process is manifested in the different coating thickness obtained with different activators. This can be attributed to the ability of the activator to dissociate during the heating period, the stability of the aluminium halide formed and its partial pressure at the aluminizing temperature. Thus, the smaller aluminide coating thickness obtained in the case of using NaCl activator can be explained by its higher degree of stability compared to NH_4Cl or AlF_3 .

The slight increase in the coating layer thickness with increasing the NH_4Cl content of the pack mixture from 1 to 6% may be due to the increase in the number of the reacting species AlCl_2 and AlCl , which act as

a gaseous medium for the transfer of Al from the pack to the substrate surface and its subsequent inward diffusion. Although the Al content in the Fe-Al component remains unchanged, the Al concentration in the pack mixture is reduced from 20.79% to 18.48% with increasing the NH_4Cl content of the pack from 1 to 12%. This may explain the slight decrease in the coating thickness obtained from powder mixture with 12% activator content.

Conclusions

The present work on the pack aluminizing of low carbon steel in the investigated range of process parameters indicated the following:

- 1) The use of Fe-Al pack excludes the formation of the brittle phases FeAl_3 and Fe_2Al_5 , and leads to the formation of Fe_3Al and FeAl intermetallic compounds.
- 2) The surface Al concentration of the coated samples increases with increasing the Al content of the pack. The temperature and time of the process increase the Al concentration at a given depth in the aluminide layer although the surface concentration remains nearly invariable.
- 3) A linear relationship is established between the squared coating thickness and the inverse absolute process temperature while the coating layer grows parabolically with time.

Acknowledgement

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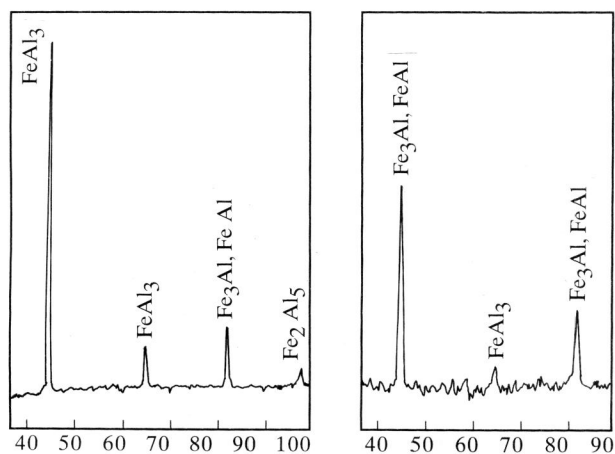


Fig. 1

X-Ray diffractograms for aluminized Δ 37 steel using $\text{Cu K}\alpha$ radiation:

- a) Pure Al pack (900°C , 4h) and
- b) Fe-Al pack (900°C , 19h).

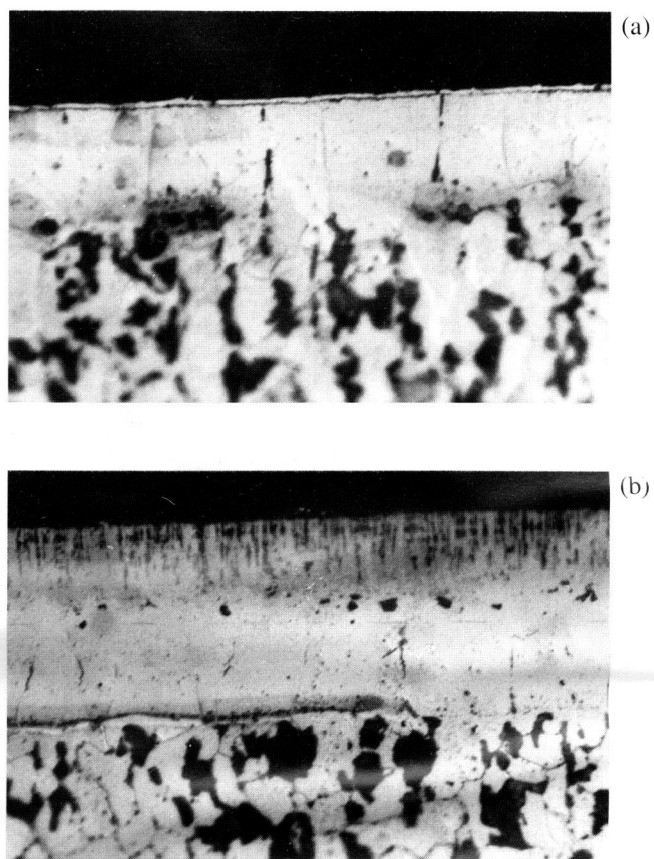


Fig. 2

Microstructure of the aluminide layers formed on Δ 37 steel in Fe-Al pack of 20% Al (a), 50% Al (b). X500

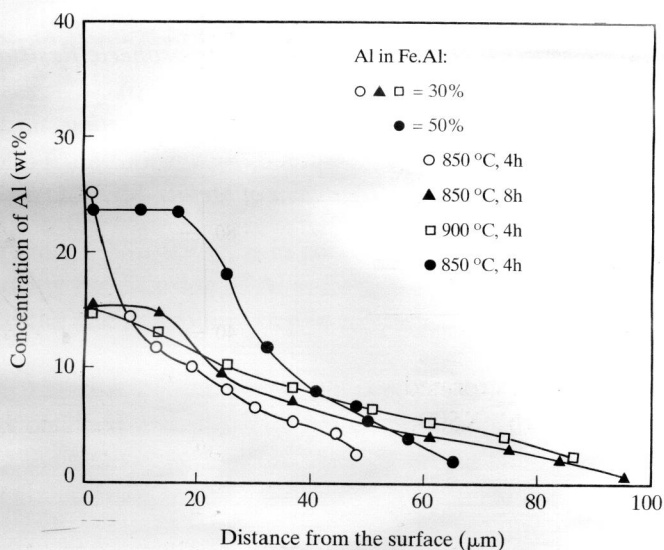


Fig. 3

Aluminium concentration profiles in the aluminide layers.

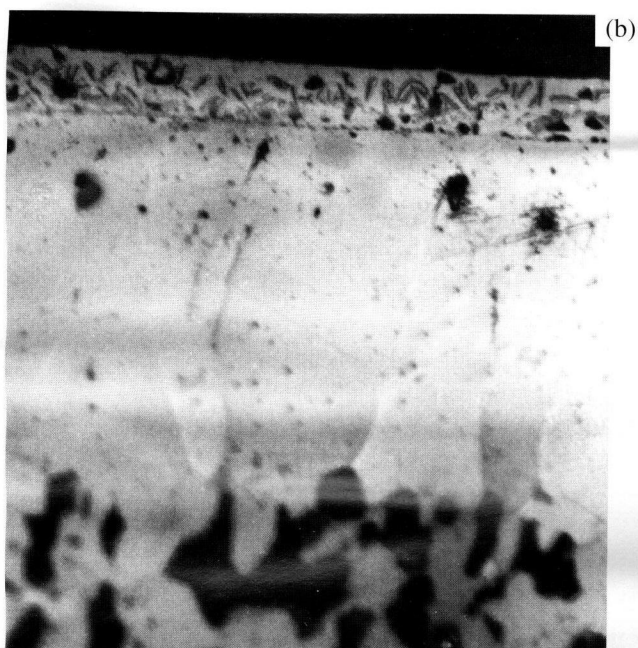
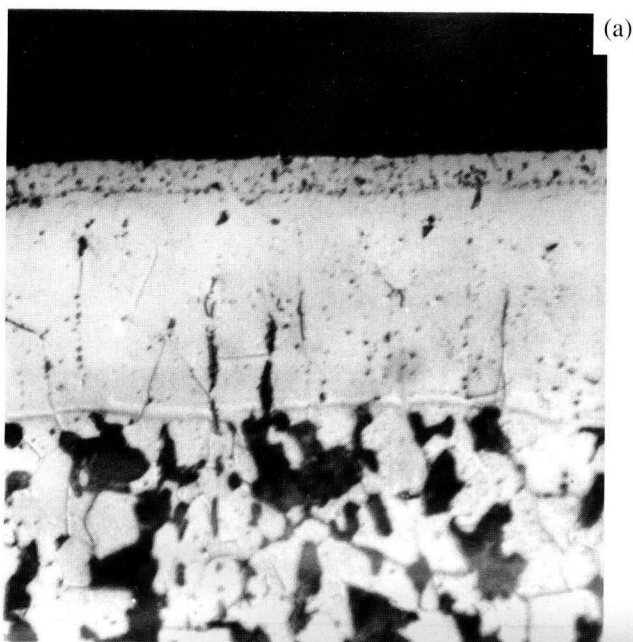


Fig. 4
Microstructure of the aluminide layers formed on Δ 37 steel at 850°C (a), 900°C (b). X500.

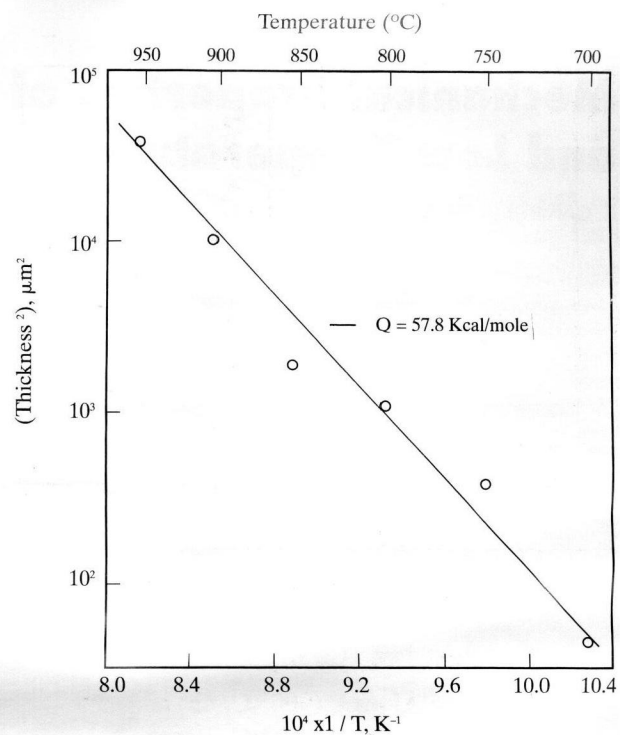


Fig. 5
Effect of temperature on the formation of aluminide coating on low carbon Δ 37 steel

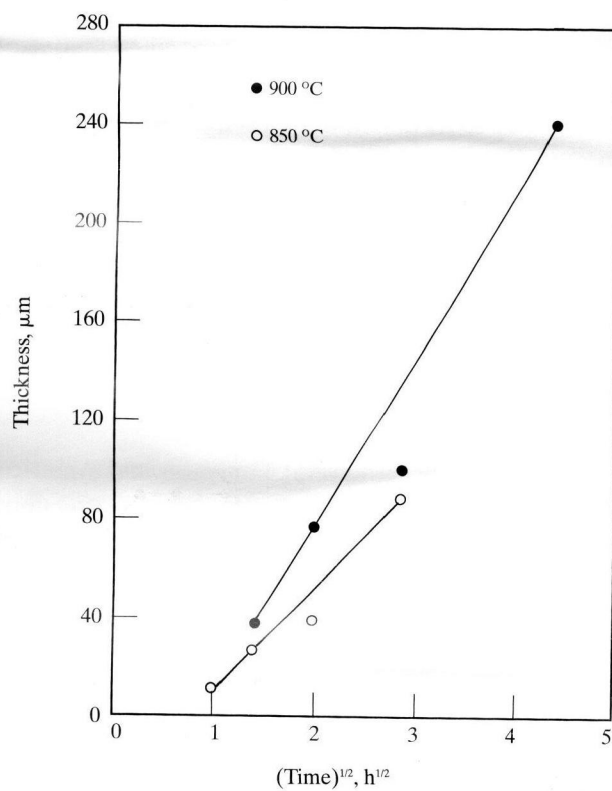


Fig. 6
Effect of time on the formation of aluminide coating on low carbon Δ 37 steel at 850°C and 900°C.