

Long-term oxidation kinetics of aluminide coatings on alloy steels by low temperature pack cementation process

Z. D. Xiang · S. R. Rose · P. K. Datta

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Abstract The long-term oxidation kinetics of the P92 steel and iron aluminide diffusion coating formed on its surface by the pack cementation process have been investigated at 650 °C over a period of more than 7000 h both in 100% steam and in air under normal one atmospheric pressure by intermittent weight measurement at room temperature. X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) techniques were used to analyse the oxidised surfaces. For the P92 steel substrate, the scale formed by oxidation is largely magnetite (Fe_3O_4) in steam and haematite (Fe_2O_3) in air. Despite this difference in the type of oxide scales formed, it was found that the long-term oxidation kinetics of the P92 steel substrate in both steam and air can be described by a logarithmic time relationship: $\Delta m_t = k_1 \ln(t/t^\circ + 1)$; the constants k_1 and t° were subsequently determined using a closest fit process for oxidations in steam and air. For the coating, the oxide scale formed in both steam and air was Al_2O_3 , which provided the long-term oxidation resistance. It was observed that the long-term oxidation kinetics of the coating in both steam and air can be best described by $\Delta m_t = \Delta m_0 + k_c t^{1/3}$; the rate constant k_c of oxidation in steam and air was then determined by the least squares

method. For both the P92 steel substrate and coating, the rate of oxidation is faster in steam than in air at 650 °C particularly in the case of the P92 steel substrate.

Introduction

Alloy steels containing typically 9–12 wt.% Cr and 1 wt.% Mo or W are high strength steels suitable for use at elevated temperatures in power generation industries [1]. Steady progress has been made in the past decade in improving the alloys' mechanical strength and creep/fatigue resistance at temperatures up to 700 °C through chemical composition modification and microstructure control [1–3]. However, because of the relatively low Cr content, the oxidation resistance of these types of steels at temperatures at or above 650 °C is not sufficient to prevent scaling or premature failure caused by oxidation particularly in steam. Thus, there has been ongoing research effort to develop efficient surface modification and/or coating deposition technologies to improve the oxidation resistance of these types of steels with an aim to increase the operating temperature of steam turbines to 650 °C and beyond and hence to significantly increase the operating efficiency and reduce the emissions of steam turbine power plants [4].

The pack aluminising process is a simple thermochemical process that can be applied to enrich the metal alloy surface with Al to form surface coatings of nickel or iron aluminide intermetallic compounds [5–8], which are known to be resistant to

Z. D. Xiang
School of Materials and Metallurgy,
Wuhan University of Science and Technology,
Wuhan, Hubei Province, P. R. China

Z. D. Xiang (✉) · S. R. Rose · P. K. Datta
School of Computing, Engineering and Information
Sciences, Northumbria University, Ellison Building, Ellison
Place, Newcastle upon Tyne NE1 8ST, UK
e-mails: z.xiang@unn.ac.uk; zhidongxiang@hotmail.com

high temperature oxidation and corrosion [9, 10]. Recent studies have also shown that these compounds are also good coating candidates for protecting alloy steels in high temperature steam [4]. However, as the pack aluminising process requires thermal activation to induce sufficient chemical reaction and diffusion kinetics, the process is normally carried out at temperatures at or above 800 °C [11–13]. Prolonged thermal treatment at these temperatures can fatally degrade the mechanical properties of the alloy steels as a result of grain coarsening and carbides precipitation [14, 15]. To minimise the possibility of such degradation, the pack process needs to be carried out at temperatures below 700 °C. In previous studies, Xiang and Datta [16, 17] had shown that this is achievable with a carefully chosen halide salt as an activator. They have demonstrated that it is technically feasible to form a uniform surface coating layer of iron aluminides on the commercial P92 steel substrate with a thickness of over 50 μm by adequately controlling the processing time or pack Al content at 650 °C. The aim of the present study is to investigate the long-term oxidation resistance of such coating in both air and steam at 650 °C. It aims to determine the long-term oxidation kinetics of both the coating and P92 steel substrate under these testing conditions. It will be shown that the rate of oxidation in steam is faster than in air at 650 °C particularly in the case of the P92 steel substrate. It will also be shown that the long-term oxidation processes of the coating and steel substrate cannot be described by the conventional parabolic rate law; instead, they were found to be a linear function of $t^{1/3}$ and $\ln(at + 1)$ respectively.

Features of the steel substrate and coating

The steel substrate used was a commercial type (P92) with a nominal chemical composition Fe-9Cr-1.0Mo-0.1C. The substrates were aluminised at 650 °C for 8 h in a pack powder mixture of a chemical composition 3Al-2AlCl₃-95Al₂O₃ (wt.%). The detailed experimental procedures of carrying out the pack aluminisation process had been presented previously [16]. The coating so formed was uniform with Cr rich precipitates. The thickness of the coating was approximately 30 μm , but this may vary from 27 μm to 31 μm due to batch-to-batch variation of the pack aluminising process. Detailed analysis had suggested that the structure of the coating consisted of an outer Fe₁₆Al₈₄ layer of approximately 8 μm and an inner FeAl₃ layer [16].

Experimental details

The oxidation tests were conducted in a tube furnace in air and in a purpose built steam oxidation rig in 100% steam at 650 °C under normal one atmospheric pressure. Figure 1 shows a schematic diagram of the steam oxidation rig, which is based essentially on the same design as reported previously [4]. It consisted of a tube furnace fitted with a stainless steel tube with an inside diameter of about 63 mm sealed at both ends. Deionised water was used to generate the steam. It was pumped at a rate of 1.48 ml/min from a reservoir through the furnace 'hot zone' via a stainless steel tube to the far side of the specimens where it emerges as steam heated to the internal temperature of the furnace. The steam then passed back over the specimens to the exhaust outlet. The exhaust steam was then cooled through a condenser and returned to the water reservoir. Care was taken to minimise the effect of residue oxygen on the test results by purging the furnace with oxygen free nitrogen before heating it up and by constantly bubbling oxygen free nitrogen through the water reservoir during the tests. The temperature in the testing zone was constantly monitored by a thermocouple, allowing the specimen temperature to be accurately controlled. The oxidation process in both air and steam was monitored by intermittent weight measurement of the specimens at room temperature. At the end of the oxidation tests, the specimens were analysed using X-ray diffraction (XRD) (Siemens Diffraktometer 5000, Cu-K α source radiation) technique to identify the oxide scales. The cross-section of

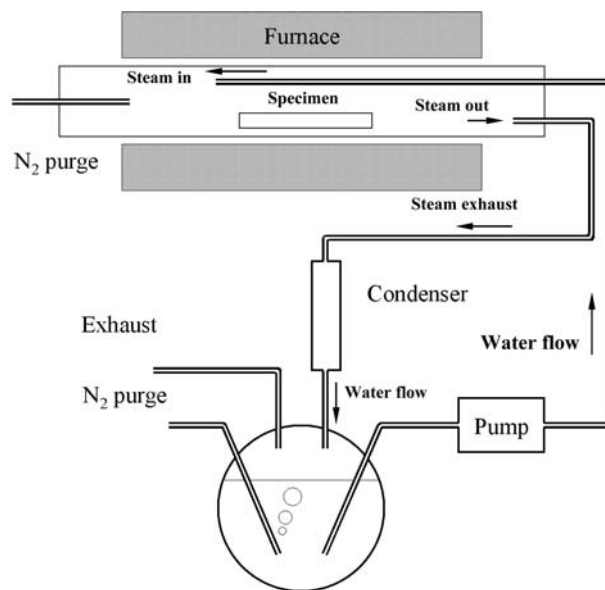


Fig. 1 Schematic diagram of the steam testing rig

the coatings were analysed using scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) and back-scattered electron imaging facilities (Hitachi S-2400) to assess the effect of oxidation on the microstructure and thermal stability of the coatings.

Results

Oxidation resistance at 650 °C

Figure 2 presents the oxidation data measured over a period of more than 7000 h in air and steam for both the substrate and coating. The nearly 100-fold difference between the vertical scales for the steel substrate (Fig. 2a) and coating (Fig. 2b) should be noted. It shows clearly that the coating is resistant to oxidation at 650 °C particularly in air. After 7089 h oxidation in air,

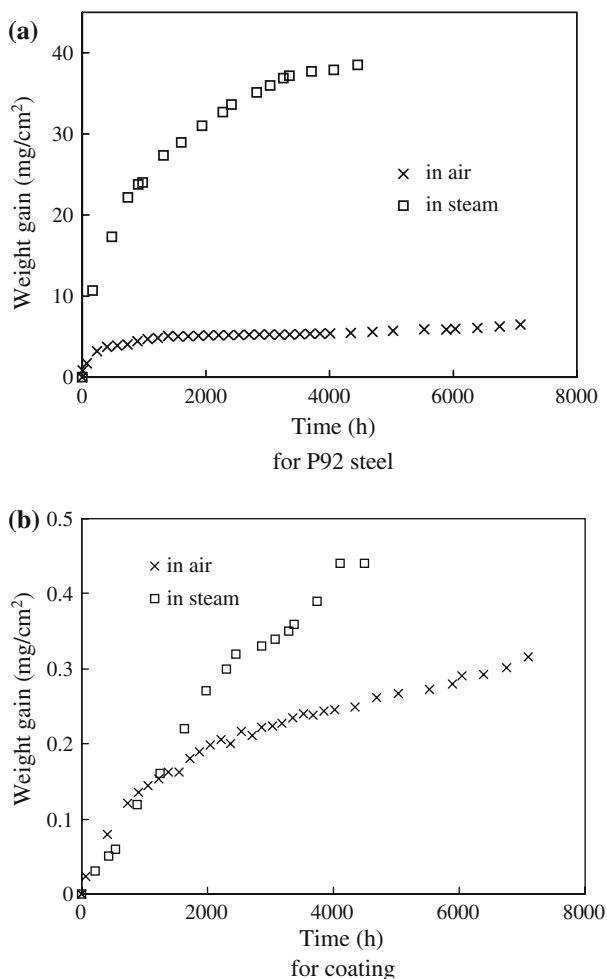


Fig. 2 Comparison of oxidation of P92-steel and coating in air with that in steam

the weight gain of the coating was only about 0.32 mg cm^{-2} without any sign of scale or coating spallation. Figure 3 shows the X-ray diffraction (XRD) pattern measured from the coating oxidised in air (the XRD pattern for the coating oxidised in steam was almost the same). It indicates that the scale formed on the coating was Al_2O_3 , which is consistent with the understanding that the iron aluminide coating is able to form a protective Al_2O_3 scale upon oxidation in oxygen containing environments [9, 10]. By assuming that the weight gain of the coating was wholly due to the formation of Al_2O_3 scale, it can be estimated that a weight gain of 0.32 mg cm^{-2} correlates to a scale thickness of approximately $1.6 \mu\text{m}$. However, this could be an overestimate by a factor of 2–2.5 because of the corrugated nature of the specimen surface [18]. Thus, the thickness of the Al_2O_3 scale formed on the coating after 7089 h oxidation in air was estimated to be less than $0.8 \mu\text{m}$. Because of the thin nature of the scale, the Al_2O_3 diffraction peaks were all very weak and those of the coating in the subsurface of the scale very strong. Figure 3 also shows that the phase of the coating was FeAl after 7089 h oxidation. This was undoubtedly converted from the original $\text{Fe}_{16}\text{Al}_{84}/\text{FeAl}_3$ coating phases as a result of the interdiffusion occurring at the interface between the coating and substrate. The XRD patterns were also measured for the steel substrate after oxidation, which suggested that the scale was haematite (Fe_2O_3) in air; but it was largely magnetite (Fe_3O_4) in steam.

Oxidation kinetics in air and steam

Figure 2 reveals that the rate of oxidation was faster in steam than in air particularly in the case of the steel substrate. The growth of oxide scale on metals or alloys is normally observed to follow a parabolic relationship [19]:

$$\Delta m_t = \Delta m_0 + k_p t^{1/2} \quad (1)$$

where Δm_t is the weight change in mg cm^{-2} at time t , Δm_0 is the initial weight gain in mg cm^{-2} due to the so called transient oxide formation and k_p is the parabolic oxidation rate constant. It is common to use the k_p value to compare the rate of oxidation for different materials tested in different environments. However, when the measured oxidation data were plotted as a function of $t^{1/2}$ (Fig. 4), only the data for oxidation of the coating in steam could be approximated fitted to a straight line over the whole oxidation period of 4454 h (Fig. 4b). All other oxidation data showed linear relationships with $t^{1/2}$ only in the early part of oxidation

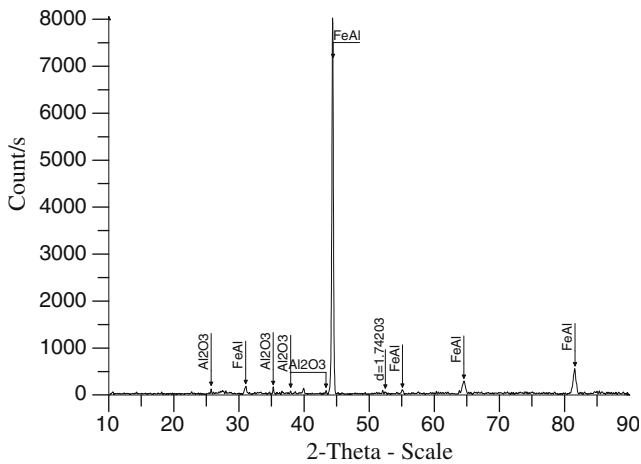


Fig. 3 X-ray diffraction pattern of the coating after oxidation in air at 650 °C for 7089 h

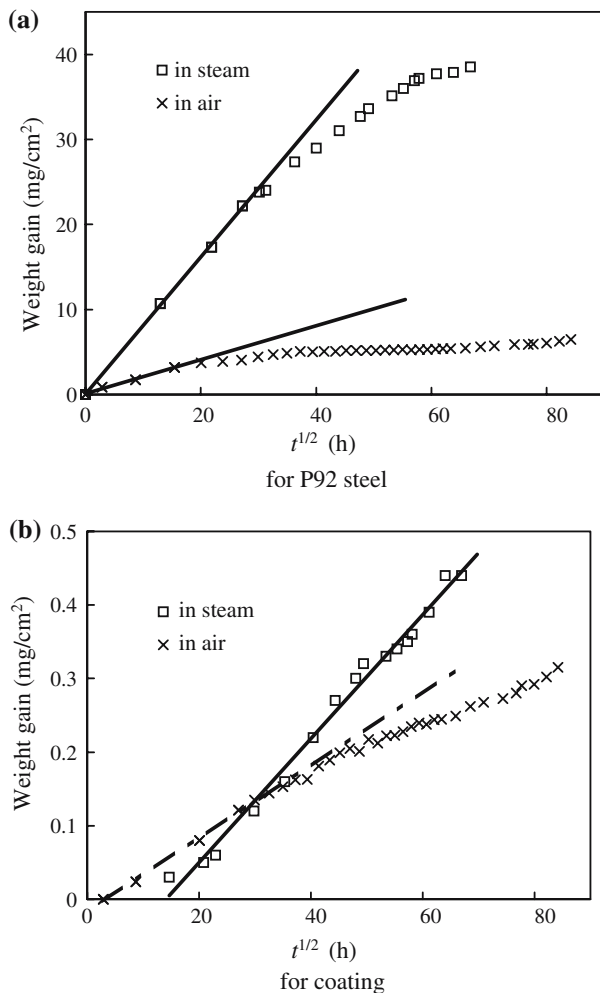


Fig. 4 Oxidation as a function of $t^{1/2}$

with divergence of a flattening feature from the straight lines becoming increasingly larger at longer oxidation times. It is clear that the oxidation periods in which

these linear relationships could be applied were relatively short in all cases, typically in the range of 700–800 h in the case of the steel substrate and less than 1250 h in the case of the coating. The straight lines in Fig. 4 are the least squares fit to the experimental data points in the corresponding linear regions. The k_p values were determined from the slopes of the straight lines, which gave the following values in $\text{mg cm}^{-2} \text{h}^{-1/2}$:

for the steel substrate, $k_p = 0.81$ in steam and 0.20 in air;

for the coating, $k_p = 0.0085$ in steam and 0.005 in air.

According to these k_p values, the rate of the oxidation was faster in steam than in air even in the early oxidation stages of both coating and steel substrate.

Thus, the parabolic oxidation kinetics defined by Eq. 1 can only be used to describe the short-term oxidation process, but cannot be applied to predict the long-term oxidation behaviour of the steel substrate and coating. On the other hand, in the case of oxidation of the steel substrate both in steam and in air, when the measured weight gains are plotted against the natural logarithms of time, it appears to show a linear relationship over the whole oxidation time of 7089 h (Fig. 5a). However, the same linear relationship does not exist in the case of oxidation of the coating (Fig. 5b).

Discussions

Oxidation kinetics of the P92 steel

The experimental evidence suggests that the rate of oxidation at 650 °C is faster in steam than in air for both the steel and coating. For the steel, it was observed that the conventional parabolic or any other power rate law of oxidation cannot be applied to describe its oxidation kinetics either in air or in steam over the whole oxidation period of more than 7000 h. Instead, a linear relationship appears to exist between the oxidation and natural logarithm of time. This oxidation behaviour differs significantly from that of the coating and indeed from those reported for many other metals or alloys, the oxidation kinetics of which are normally observed to follow the parabolic or cubic rate law of oxidation [19–21]. However, it should be noted that all the previously reported kinetics were determined from oxidation data measured over only a short oxidation period of usually less than 300 h. Over such short oxidation time, Fig. 4 clearly shows that the parabolic rate law of oxidation can be applied to describe the oxidation kinetics of the steel substrate as

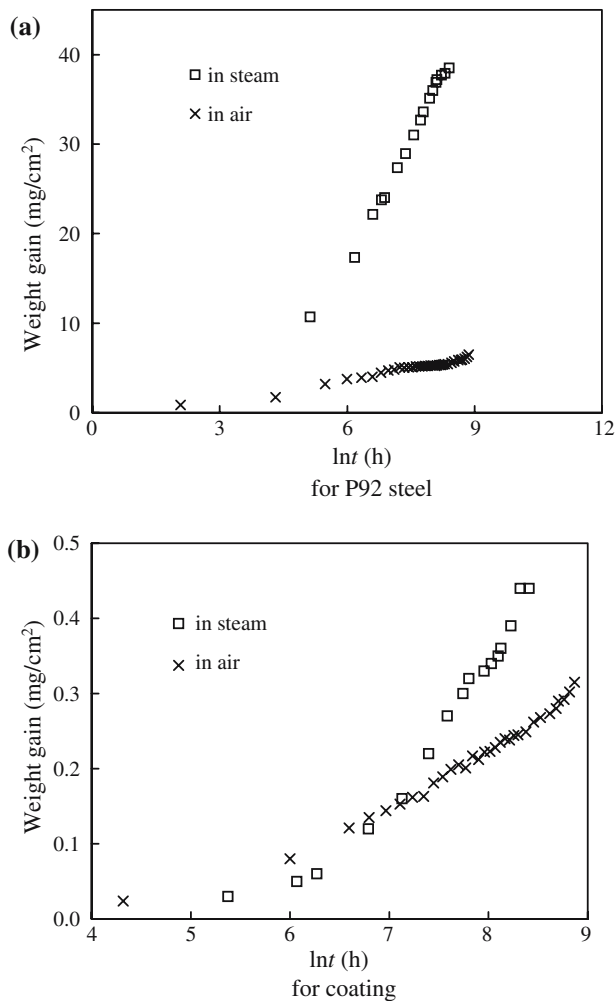


Fig. 5 Oxidation as a function of $\ln t$

well as the coating both in steam and in air; however, it can produce serious errors when applied to predict their long-term oxidation behaviour.

There have been few studies in the literature reporting the logarithmic kinetics for the oxidation of metals or alloys. The earliest experimental work that convincingly demonstrated the linear relationship between oxidation and logarithm of time was that reported by Vernon, Akeroyd and Stroud on the oxidation of zinc in air in the temperature range from 25 °C to 400 °C [22]. In the same investigation, they also re-examined the previously published kinetic data of iron oxidation in air and found that a linear relationship also existed between the oxidation and logarithm of time particularly at longer oxidation times and at higher temperatures. More recently, the present authors had also observed the logarithmic kinetics for oxidation of the TiAl_3 coating formed on γ -TiAl by pack cementation over the whole oxidation period of more than 6200 h at 800 °C [23].

A number of mechanisms had been suggested in an attempt to advance a meaningful theoretical model to account for the observed logarithmic oxidation behaviour of zinc and iron [22]. A particularly useful mechanism is probably the one suggested by Mott [18] who was able to show that the oxidation process could follow a logarithmic relationship with time if it is assumed that the oxidation is controlled by diffusion of electrons for the growth of thin films or by the re-crystallisation process of oxide scales for the growth of thick films. In the latter case, it can be derived that

$$\Delta m_t = k_1 \ln(\alpha t + \beta) \tag{2}$$

where k_1 , α and β are all constants; k_1 and a are in the unit of mg cm^{-2} and h^{-1} respectively. Noting that at the beginning of an oxidation process when $t = 0$, $\Delta m_t = 0$, which gives $\beta = 1$, one can have

$$\Delta m_t = k_1 \ln(at + 1) \tag{3}$$

Equation (3) predicts that a plot of Δm_t against $\ln(at + 1)$ is a straight line through the origin. Using a closest fit process, the constants k_1 and a were determined for oxidation of the steel substrate; the results are as follow:

$$\text{for oxidation in air, } \Delta m_t = 0.86 \ln(0.165t + 1) \tag{4}$$

$$\text{for oxidation in steam, } \Delta m_t = 10.35 \ln(0.0099t + 1) \tag{5}$$

where Δm_t is in mg cm^{-2} and t in h. The Eqs. (4) and (5) are validated by plotting Δm_t against $\ln(at + 1)$ in Fig. 6; the points are the experimental data and straight lines that pass through the origin represent the Eqs. (4) and (5). It confirms that the kinetics defined by Eq. (3) can be applied to describe the scale growth process over the whole oxidation period studied.

Clearly, the physicochemical significance of the constants k_1 and a requires detailed consideration. In the case of zinc oxidation in air, Vernon, Akeroyd and Stroud [22] had shown that k_1 increased, but a remained constant, with oxidation temperature at temperatures higher than 225 °C at which the oxide scale started to change its physical state from amorphous to crystalline. Thus, it seems reasonable to use the k_1 value as a rate constant to directly compare the oxidation rate of the same metal under different oxidising environments. Equations (4) and (5) show that the k_1 value in steam is more than 12 times that in air at 650 °C, confirming that steam is a much more severe oxidation medium than air for the steel substrate. Eqs. (4) and (5) also show that the constant a is

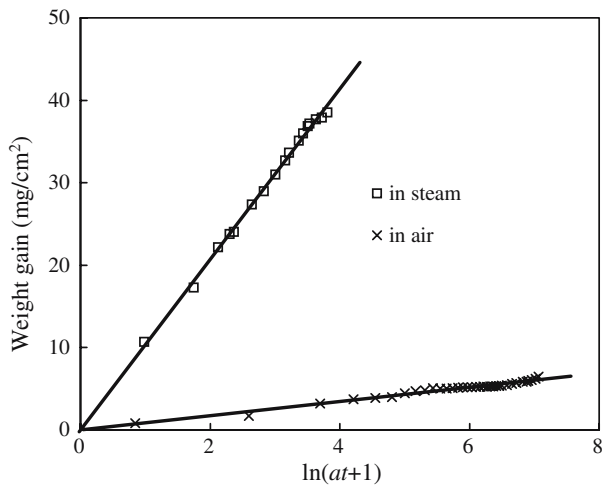


Fig. 6 Oxidation of P92-steel as a function of $\ln(at+1)$ at 650 °C

approximately 0.0099 h^{-1} in steam and 0.17 h^{-1} in air at 650 °C for the steel substrate. Hence, like the constant k_1 , it also strongly depends on oxidising media; but in contrast to k_1 , it is much lower in steam than in air. However, if the Eq. (3) is presented in the following form by defining $t^\circ = 1/a$:

$$\Delta m_t = k_1 \ln(t/t^\circ + 1) \quad (6)$$

where t° is another constant in the unit of h, one can easily show that t° is approximately 101.0 h in steam, which is much higher than 5.9 h in air for the steel substrate at 650 °C. Hence, Eqs. (4) and (5) can be rewritten as:

$$\text{for oxidation in air, } \Delta m_t = 0.86 \ln(t/5.9 + 1) \quad (7)$$

$$\text{for oxidation in steam, } \Delta m_t = 10.35 \ln(t/101.0 + 1) \quad (8)$$

It appears that both constants k_1 and a are required to describe the oxidation kinetics of the steel substrate in different oxidation media. Nevertheless, detailed studies are required to determine whether the constant a is independent of oxidising temperature in the same oxidising medium as observed in the case for high temperature oxidation of zinc in air [22].

Oxidation kinetics of the coating

The results presented in Fig. 2 demonstrate that the coating can provide long-term oxidation resistance for the steel substrate both in steam and in air at 650 °C. This long-term oxidation resistance is provided by the formation and slow growth of Al_2O_3 scale in both oxidising media. Despite the demonstrated oxidation resistance of the coating under the testing conditions

studied, the growth rate of the Al_2O_3 scale in steam appears to be higher than in air (Fig. 2). The conventional parameter used to quantify the growth rate of the Al_2O_3 scale under different oxidising conditions is the parabolic oxidation rate constant k_p defined in Eq. (1). However, Fig. 4b shows that the parabolic kinetics can be approximately applied only to the oxidation of the coating in steam over the whole oxidation period of 4454 h. For oxidation of the coating in air, only the early part of the oxidation data of less than 1250 h can be approximately fitted to the parabolic kinetics with negative departure becoming increasingly larger at longer oxidation times. This “flattening” phenomenon at longer oxidation times has been noted also for other alumina scale forming alloys and the inadequacy of the parabolic kinetics in describing the long-term scale growth behaviour of these alloys has been discussed in recent years by a number of investigators who have attempted to account for this phenomenon by taking into account the effects of the grain-boundary diffusions and grain size growth of the oxide scales in the direction of grain growth [20, 21]. It has been subsequently proposed that for alumina scale forming alloys such as NiAl or steels containing typically 5–6 wt.% Al the long-term growth kinetics of the alumina scales at high temperatures can be better described by a cubic rate relationship of the type:

$$\Delta m_t = \Delta m_0 + k_c t^{1/3} \quad (9)$$

where k_c is the cubic rate constant of oxidation in $\text{mg cm}^{-2} \text{ h}^{-1/3}$. The k_c values under different oxidation conditions can be obtained from the slope of the plot of Δm_t against $t^{1/3}$. Figure 7 shows two such plots, one for oxidation of the coating in air over the whole oxidation period of 7089 h and another for oxidation of the coating in steam at oxidation times longer than 400 h. Both plots show a straight line, demonstrating the validity of the cubic oxidation kinetics defined by Eq. (9) in describing the long-term oxidation process of the coating both in steam and in air. The least squares fit gives:

$$\Delta m_t = 0.045 t^{1/3} - 0.31 \text{ for oxidation in steam } (t > 400\text{h}) \quad (10)$$

$$\Delta m_t = 0.019 t^{1/3} - 0.046 \text{ for oxidation in air } (t > 70\text{h}) \quad (11)$$

It is significant to note that the k_c value for oxidation of the coating in steam is more than twice the value in air, suggesting that steam, compared with air, is a more severe oxidising medium for the coating at 650 °C.

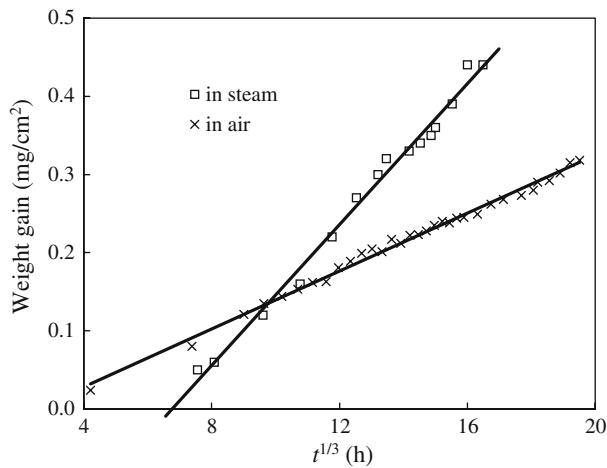


Fig. 7 Oxidation of the coating as a function of $t^{1/3}$ at 650 °C

Thermal stability of the coating

The phase in the outmost surface of the original coating was $Fe_{18}Al_{84}$ [16], which was transformed to FeAl after 7089 h oxidation in air (Fig. 3). This was primarily as a result of interdiffusion taking place at the coating/substrate interface during the test, which led to the depletion of Al in the coating and could eventually cause the coating to lose its oxidation resistance. The effect of this interdiffusion process is further illustrated in Fig. 8 where the Al and Fe concentration profiles in the coating after isothermal annealing for 1132 h at 650 °C under the Ar atmosphere are compared with those in the original coating. It suggests that for a coating with a thickness of about 30 μm , the $Fe_{18}Al_{84}$ to FeAl transformation process had been completed in 1132 h. Thus, the oxidation resistance of the coating at oxidation times longer than 1132 h was provided by the FeAl phase and this phase remained stable in the outmost surface of the coating in the following oxidation period up to 7089 h. However, it is expected that the FeAl phase will eventually degenerate to the Fe_3Al phase as a result of the continued interdiffusion process at 650 °C. Further research is in progress to quantify this interdiffusion process and to develop a meaningful model for predicting the lifetime of the coating.

Conclusions

The oxidation rate is faster in steam than in air at 650 °C for both the P92 steel substrate and the iron aluminide coating formed on its surface by the pack

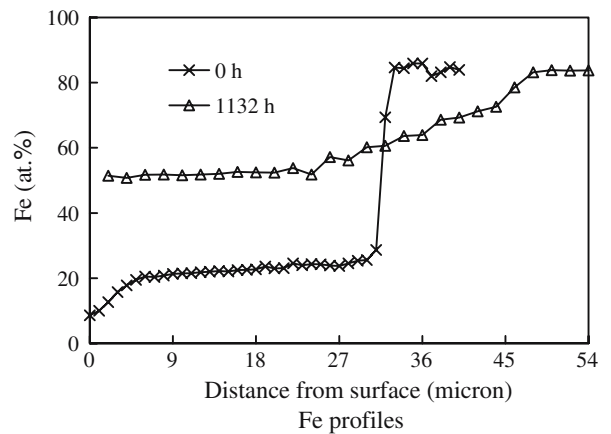
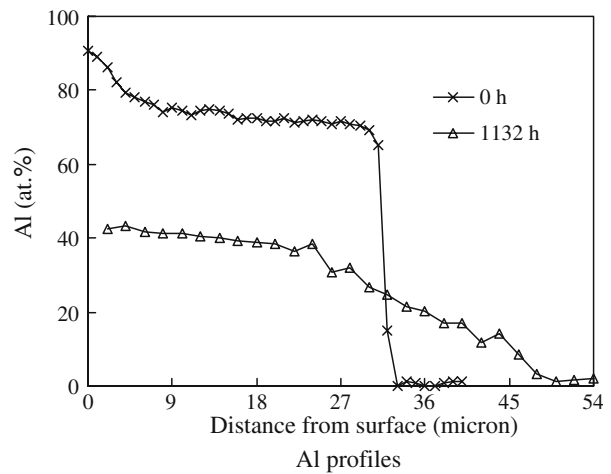


Fig. 8 Al and Fe concentration profiles in the coating before and after 1132 h isothermal annealing at 650 °C under Ar atmosphere

cementation process. Even so, the coating is resistant to oxidation and can provide long-term protection for the substrate both in steam and in air at 650 °C. For the P92 steel substrate, the long-term oxidation kinetics both in steam and in air at 650 °C follows a logarithmic time relationship $\Delta m_t = k_1 \ln(at + 1)$ with the scale oxide formed being mostly magnetite (Fe_3O_4) in steam and haematite (Fe_2O_3) in air. The oxidation resistance of the aluminide coating both in steam and in air at 650 °C is afforded by the formation of alumina scale, the long-term growth kinetics of which cannot be described by the conventional parabolic rate law, but by $\Delta m_t = \Delta m_0 + k_c t^{1/3}$ in both steam and air at 650 °C.

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