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Relationship between pack chemistry and aluminide coating formation for low-temperature aluminisation of alloy steels

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Abstract

A theoretical analysis is provided to relate the coating layer growth kinetics to the pack chemical composition and processing conditions under a set of defined thermodynamic and kinetic conditions for aluminising alloy steels at temperatures below 700 °C in an effort to increase their high-temperature oxidation resistance whilst maintaining their microstructure and hence mechanical strength and creep resistance. A series of experiments were subsequently carried out on a type of commercial alloy steel P92 (12Cr–1Mo) in $AlCl_3$-activated packs containing Al as the depositing source and Al_2O_3 as inert filler with the aluminising temperature varying from 500 to 700 °C, pack Al content from 1 to 30 wt.% and aluminising time from 1 to 16 h to determine the effects of these parameters on the coating growth kinetics and microstructure and hence to check the validity of the assumptions made in the theoretical analysis. The applicability of this analysis in the cases of aluminising steels using different halide salts as activators is also assessed, which highlighted the limited choice of activators available for aluminising alloy steels in the low-temperature range concerned.

Keywords: Iron aluminide; Steels; Coatings; Pack cementation process

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1. Introduction

The power generation industries are facing increasing demands to improve thermal efficiency in order to meet more stringent environmental regulations on carbon gas emissions. Thus, for steam turbine power generators, the steam operating temperature is expected to increase from the current 550–580 °C to at least 650 °C in the future. This requires suitable structural steels with sufficient high-temperature creep/fatigue strength and oxidation and corrosion resistance. Much progress has been made in improving the (9–12)Cr–1Mo (wt.%) type of alloy steels' mechanical strength and creep/fatigue resistance at temperatures up to 700 °C through modifying alloy steel chemical composition [1,2]. However, the oxidation resistance of these types of steels in supercritical steam at these temperatures is poor, as the Cr content in these steels is not sufficiently high to prevent rapid oxide scale growth [3]. However, this property can be improved by enriching the surface of the steels with Al to form iron aluminide coatings. Recent studies have shown that iron aluminides are highly oxidation and corrosion resistant and can provide an effective protection for alloy steels in high-temperature steam due to their ability to form a slow-growing alumina (Al_2O_3) scale [3–5], which, unlike silica and chromia scales, remains chemically stable in supercritical steam at high temperatures.

The pack cementation process may be applied to form aluminide coatings on alloy steels [6–13]. The process has processing simplicity and flexibility required for treating

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components of various dimensions and geometries. However, a key limitation of the process is that it requires thermal activation to generate sufficiently fast chemical reaction and interdiffusion kinetics. As such, the process is normally applied at temperatures above 750 °C. Thermal treatment at these temperatures for long periods, typically 6–30 h in a pack aluminising cycle, can fatally degrade the mechanical properties of alloy steels as a result of microstructure changes associated with grain coarsening and carbide precipitation [14,15]. To prevent such degradation, the aluminising process needs to be carried out at temperatures below 700 °C. For some types of steels such as martensitic steels, the maximum allowed processing temperature is not much higher than 650 °C, which is significantly below the melting point of Al (~660 °C). This imposes a severe restriction on the applicability of the pack cementation process.

A number of systematic studies have been reported in the literature on the aluminide coating formation on metals in the pack aluminising process in relation to determining the effects of processing conditions on the growth kinetics and resultant microstructures of the coatings. Particularly notable are those reported by Levin and Cave on a nickel-based superalloy at 982–1149 °C [16], Wang, Seigle and co-workers on nickel and Ni–Cr alloys and pure Fe at 800–1150 °C [17–20], Kung and Rapp on pure Fe at 900 °C [13], Akuezue and Stringer on Fe–Cr alloys at 850–1000 °C [21], Soliman et al. on carbon steels at 750–900 °C [11], Levin et al. on pure Fe at 900 °C [12], and Xiang et al. on a nickel-based superalloy at 800–1100 °C [8]. It can be seen that all these previous studies were made at temperatures above 750 °C. Systematic studies on aluminising alloy steels in the temperature range below 700 °C are almost non-existent in the literature. However, it is considered that, when the pack is properly activated, sufficiently fast growth of an Fe_2Al_5 coating on alloy steels would be achievable in the temperature range considered, as it is known that Al diffusion is sufficiently fast even at 700 °C in the Fe_2Al_5 phase due to its defect structure containing large numbers of aluminium vacancies [22]. Indeed, the authors demonstrated in a previous study [23] that, by selecting a suitable activator, it is technically feasible to grow a layer of Fe_2Al_5 coating at 650 °C on T22 alloy steel (2.25Cr–1Mo) to a sufficient thickness suitable for industrial applications. In this work, an analysis is provided on the theoretical basis for controlling the formation and growth process of iron aluminide coatings on alloy steels at these low temperatures. Also, an equation is derived that relates the coating growth to the pack chemistry as defined by the pack chemical composition and processing conditions. The validity of this analysis is subsequently confirmed by experiments.

2. Theoretical analysis

The pack aluminising process is essentially a chemical vapour deposition (CVD) process activated by halide salts. Two interrelated processes take place simultaneously in the pack at high temperatures. One is the process of chemical reaction to generate aluminium halide vapours and ensuing migration of these vapours to the metal surface; we term this process as the activation/migration process. Another is the process of depositing Al through the reduction reactions of aluminium halide species on the metal surface and subsequent solid-state interdiffusion between the deposited Al and elements in metal substrates; we term this process as the deposition/diffusion process. The formation mechanism, growth kinetics, phase and microstructure of the coatings produced on the metal surface depend strongly on the chemical composition and partial pressure level of vapour species generated in the pack at high temperatures. For instance, in the case of Ni-based superalloys, it is a common experimental observation [24] that the coating grows via an outward Ni diffusion mechanism and the corresponding phase formed is NiAl deficient in Al when the aluminising temperature is sufficiently high and the partial pressure of Al halide vapours or the activity of Al in the pack is adequately low; in contrast, when the aluminising temperature is suitably low and/or the partial pressure of aluminium halide vapours or the activity of Al in the pack is sufficiently high, the coating forms through an inward Al diffusion mechanism and the resultant phase formed could be NiAl rich in Al or Ni_2Al_3. In the case of pure iron or steel, it is observed that coatings form largely through inward Al diffusion regardless of the chemical composition of the packs or deposition conditions used [11–13,23].

For the activation/migration process, Levin and Caves [16] have shown that the amount of Al transported through the pack by the migrating aluminium halide vapours (AlCl, $AlCl_2$, $AlCl_3$, etc.) and subsequently deposited on the metal surface of an unit area (m in mg cm^{-2}) at a time interval t can be given by

$$m = k_g t^{1/2} \tag{1}$$

$$k_g = \left(\frac{2n\varepsilon M_{Al}}{lRT} \sum D_i (p_i - p_{i0}) \right)^{1/2} \tag{2}$$

where k_g is the parabolic rate constant of vapour phase migration of Al halide species through the pack to the specimens surface, ε and l the correction factors for pack porosity and pore length, respectively, n the Al concentration (g cm^{-3}) in the pack, M_{Al} the atomic weight of Al, R the gas constant, T the absolute temperature, D_i the diffusivity of the vapour species in the pack and p_i and p_{i0} the partial pressures of the aluminium halide vapour species in equilibrium with A or master alloy in the bulk pack and with Al at the outmost surface of the formed coating, respectively. The driving force for transporting Al by the migration of aluminium halide vapour species through the bulk pack to the metal substrate surface is clearly the difference in the partial pressures of aluminium halide vapours between those in equilibrium with the Al or master alloys in the bulk pack and those in equilibrium with the outmost surface of the formed coating. Levine and Caves and other