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Rare-earth modified chromium–aluminide coatings applied by pack cementation method on low-alloy steels

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In metallurgical practice the presence of a minor amount of certain elements can induce significant changes in a material's physical, mechanical and chemical properties. In this paper we present the nature, morphology and properties of protective coatings containing Cr, Al and minor amounts of a rare earth element, applied on 2.25Cr–1 Mo low-alloy steel. The coating technology, pack cementation, was used to achieve the simultaneous deposition of the coating elements in a one step process. Cyclic oxidation, conducted in air at 800 °C, induced thermal stresses on the alloy samples, promoting the tendency of the oxide scales formed to spall. The rare earth modified coatings, under these conditions showed the beneficial effects of the rare earth addition. These coatings, upon exposure, developed an adherent oxide scale which had better properties, and retarded the alloy's degradation. This lead to a significant reduction in the overall oxidation rate.

1. Introduction

Iron-based alloys, especially those with low alloying, are the principal materials used in utility boilers and petrochemical plants due mainly to their low cost and good mechanical properties. Low-alloy steels operating in chemically reactive environments and at temperatures that exceed 500 °C are susceptible to high temperature oxidation, both high and low temperature hot corrosion and thermal fatigue especially under cyclic conditions.

To improve their surface stability, and hence their resistance to environmental degradation, whilst maintaining good fabrication and mechanical properties, the surfaces of these alloys may be enriched in both chromium and aluminium. These elements facilitate the formation of protective chromia and alumina scales, which are however sensitive to thermal cycling, and tend to spall.

Since it was discovered about 60 years ago, [1] that trace additions of oxygen active elements like Y, La and Ce, to alloys that form Al or Cr oxide scales upon exposure at high temperatures, have a strong beneficial effect on the oxidation behaviour of these materials, many studies have been performed to further investigate this effect which has become known as the reactive element effect (REE) [2–4].

Pack cementation is a coating technology which is basically an *in situ* self-generated chemical vapour deposition (CVD) process. In addition to being cost effective, it has the advantage of being able to be applied to a wide variety of metal parts including those with complex geometries. The parts to be coated are buried in a reactive powder (source of the coating elements), contained inside a thermodynamically semi-closed system and isothermally heated at elevated temperatures for a chosen period of time. Successive coating steps are often necessary in current commercial practice to deposit more than one element.

However there is an economic incentive for a one step process. For successful simultaneous deposition of Cr and Al, recent studies [5, 6], have shown that in order to achieve the required partial pressures of metallic halides in the pack a Cr–Al masteralloy composition with at least 90 wt % Cr (balance Al), must be used.

The purpose of this study is to develop an oxidation/corrosion resistant Cr–Al surface coating produced by simultaneous deposition of the constituent elements and modified with a reactive element (RE) suitable for application to low alloy steels. The effect of the RE addition on the high temperature performance of these alloys is also evaluated.

2. Experimental procedure

Rectangular specimens with dimensions of about 1.5 × 1.0 × 0.5 cm were machined from low alloy steel, 2.25Cr–1.0Mo. They were ground down to 500 grit and placed in packs with the appropriate powders. The pack powder mixtures consisted of a Cr–Al masteralloy, an NH_4Cl activator and alumina powder as a filler. In selected packs some alumina was replaced by HfO_2 powder, which acted as a source of reactive Hf. The process temperature was 1150 °C and the duration was 4–12 h. The period of the cyclic oxidation test in air was 60 min in a furnace at 800 °C and cooling to room temperature in 15 min.

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TABLE I Summary of results obtained for packs A and B of the pack cementation coating processes of 2.25Cr–1Mo steel substrate

		Coating composition (at %)					
Pack	Coating	Cr	Al	Hf	Fe	Weight gain (mg cm^{-2})	Thickness (μm)
A	Cr–Al	25.5	4.7	–	67.6	12.9	90
B	Cr–Al–Hf	18.3	2.6	0.2	77.1	11.6	80

Metallographic examination and analysis was performed by optical and also scanning electron microscopy (SEM). Chemical compositions were determined by energy dispersive X-ray spectrometry (EDS).

3. Results and discussion

Table I, summarizes the results obtained for two selected packs A and B and in Fig. 1(a and b) is shown a cross-section of part of the coating (about 15 μm from the surface), obtained from pack B, together with the results of EDS analysis.

Two objectives when adding the RE are (i) to achieve a uniform finely dispersed distribution in the alloy prior to oxidation and (ii) to control the amount of the addition [7, 8]. Hf, when added into the bulk of the alloy, primarily for grain boundary strengthening but also for oxide scale adherence has a marked influence on workability which in turn is concentration sensitive [9, 10]. It is clear from our results, that the co-deposition of Cr and Al, and the deposition of small amounts of Hf into the surface of the alloy, in a one step process was achieved. We have therefore avoided the adverse effects on workability associated with bulk additions. Hf was uniformly distributed in the coating, except for a layer of about (2 μm thickness) marked as D in Fig. 1a, which was found to be more rich in Hf, Fig. 1b.

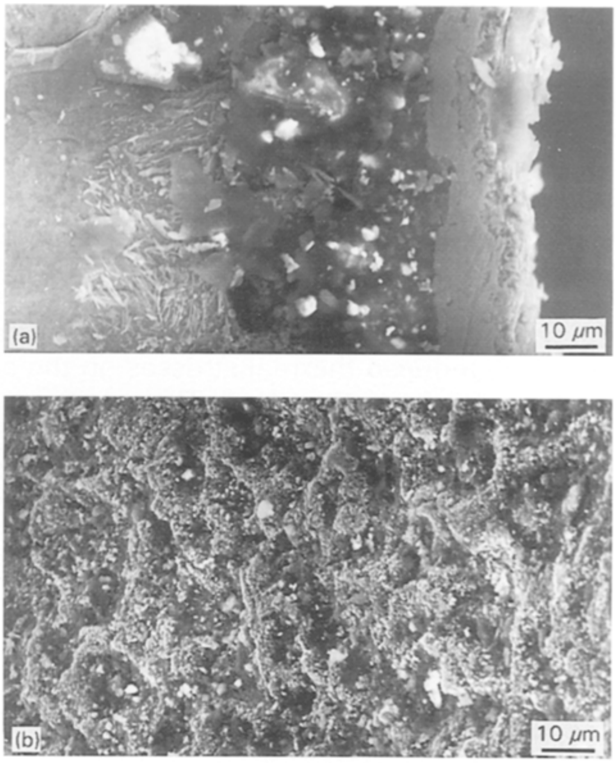

Figure 2 SEM micrographs of Hf modified Cr–Al coating on 2.25Cr–1Mo steel. (a) Cross-section microstructure, (b) surface morphology, after 400, cycles of cyclic oxidation tests of 60 min duration at 800 °C in air.

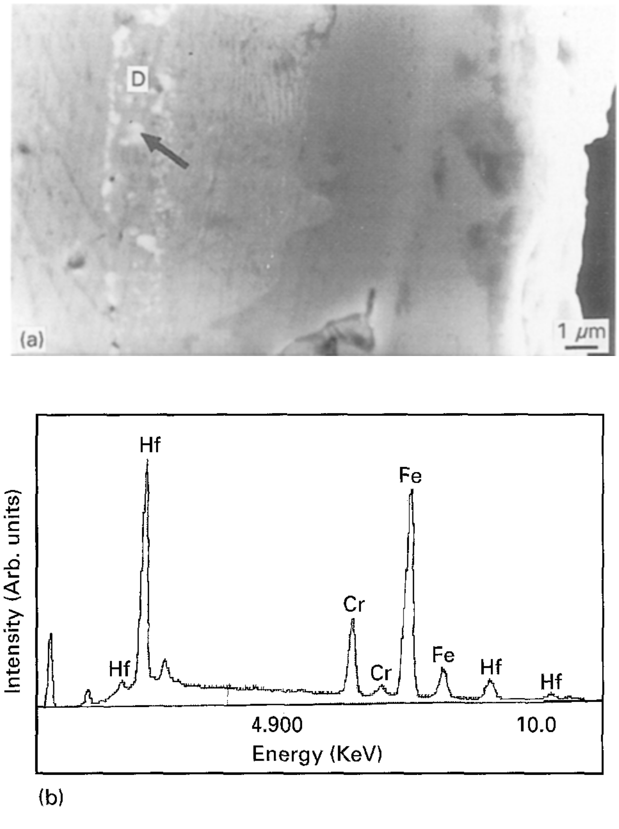

Figure 1 (a) SEM micrograph of part (about 15 μm from the surface) of the Hf modified Cr–Al coating on 2.25Cr–1Mo steel. (b) EDS analysis of a particle indicated by the arrow in the layer marked D, showing that it is a Hf rich phase.

Cyclic oxidation test results for three sets of specimens are presented in Fig. 4. For a protective coating to be effective, a thin, compact and adherent oxide scale should be formed on the onset of exposure and thereafter should slowly grow and be thermodynamically stable. The Hf modified chromium-aluminized alloy had excellent oxidation kinetics as demonstrated by the cross-sectional microstructure, surface morphology and the weight change behaviour compared to the chromium–aluminized, and the uncoated alloys.

This marked improvement of high temperature resistance of the Cr–Al–Hf coating due to Hf addition was very significant taking into account the coating thickness and obtained compositions which are shown

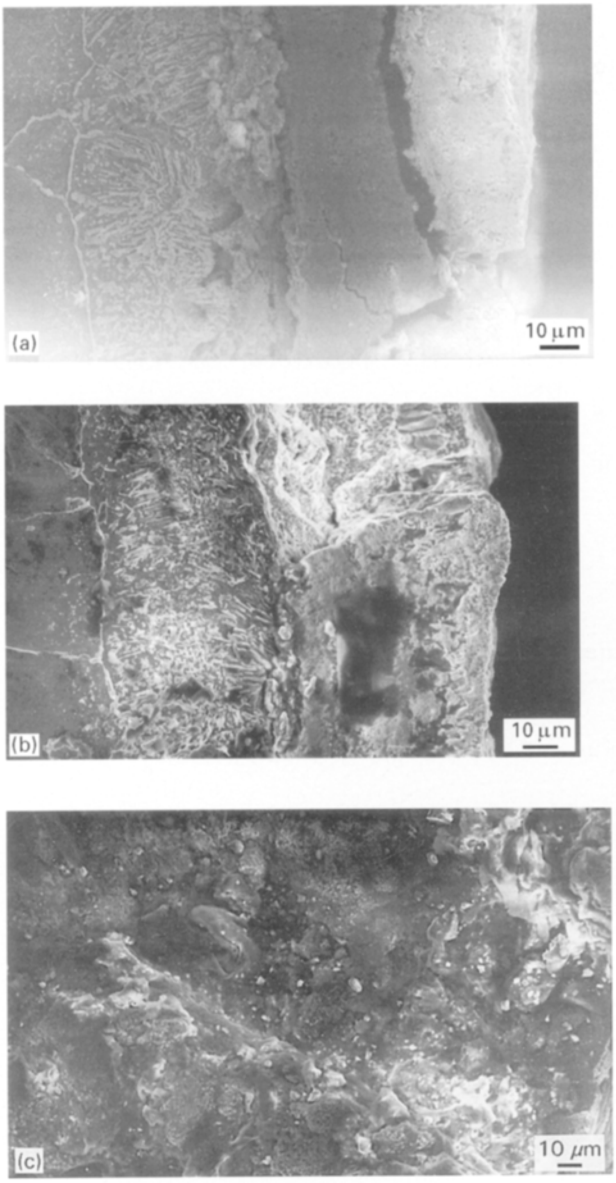

Figure 3 SEM micrographs of Cr–Al coatings on 2.25Cr–1 Mo steel. (a) and (b) Cross-section microstructures, (c) surface morphology, after (a) 225 (b) and (c) 400 cycles of cyclic oxidation tests of 60 min duration at 800 °C in air.

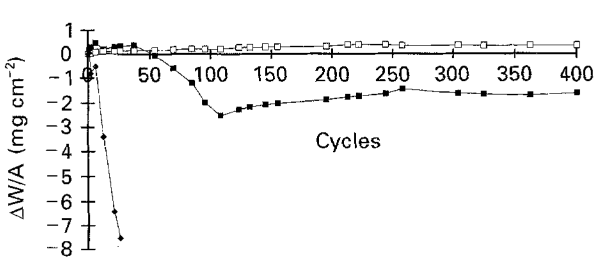

Figure 4 Weight change versus number of cycles of coated and uncoated 2.25Cr–1Mo steel under thermal cycling conditions (heating: 60 min at 800 °C, cooling: 15 min in air.) Data is shown for; (■) Cr–Al, (□) Cr–Al–Hf and (◆) uncoated.

in Table I. The coatings had almost the same thickness, so the through thickness-cracking, the tendency to crack on cooling, was taken to be the same for both coatings. The Cr–Al coating started spalling heavily after only 40 cycles, Fig. 4. By the end of the oxidation test, extensive cracking of the oxide scale and the coating layer immediately below it, had taken place, Fig. 3(a–c). Minimal spalling was observed for the Cr–Al–Hf coating during the entire cyclic oxidation test, although in terms of composition (lower Cr and Al content) it was expected to have reduced resistance to oxidation for prolonged exposure. This is because oxidation protection by a Cr–Al coating is based on the synergistic interaction of Cr and Al to form both Cr_2O_3 and Al_2O_3 on the surface of the alloy-coating system. These oxides must be continuously replenished. Therefore Cr and Al composition amongst other factors will determine the coating's long term performance.

However, the most important consideration, once the oxide scale has been formed is how well it adheres to the alloy-coating surface. Coating composition had a direct relationship to oxide scale growth and grain size. Hf contents led to slower scale growth indicating lower oxidation rates. In addition, Hf influenced the growth mechanism to form oxide scales with smaller grain sizes, Fig. 2b. This should promote better scale adhesion [10]. The RE addition probably acted as a physical barrier to outward diffusion of Cr and Al cations, by segregating into grain boundaries. The low oxidation rates produced a thin oxide scale which had increased fracture toughness during thermal cycling due to lower thermal mismatch stresses, as was demonstrated by the weight change behaviour and metallographic analysis.

For alloy specimens with a Cr–Al–Hf coating, the weight gains after 400, 60 min cycles were below 0.4 mg cm^{-2}, which compares well with cyclic oxidation results obtained by other investigators [6], for similar coatings, but without RE additions and for longer thermal cycles. The steady-state oxide growth was reached at the 220 cycle mark. The only evidence of degradation was the deformation of both the coating, Fig. 2a, and the oxide scale, Fig. 2b. Although the surface morphology revealed several local spots of repetitive formation and spalling of the oxide scales, weight change measurements showed that this did not amount to any substantial material removal.

4. Summary

Based on the results obtained and observations made during experimentation, it can be concluded that it was possible to introduce small amounts of the rare earth element Hf, simultaneously with Cr and Al in to the surface of a low alloy steel, by pack cementation. During the thermal cycling test, the growth, structural and thermal stresses generated were relieved through coating and oxide scale deformation and through cracking and spalling of the oxide scale. Hf favoured the less destructive modes of stress relief, that is, coating and oxide scale deformation and inhibited scale cracking and spalling. In the absence of Hf all modes of stress relief were operative. Therefore the rare earth modification of the Cr–Al coating, led to a substantial improvement in the coating's resistance to high temperature cyclic oxidation.

In this paper, a brief presentation of the successful deposition of three elements Cr, Al and Hf in a single step process by halide-activated pack cementation technique on the surface of a low-alloy steel, and preliminary testing is made. In a future paper, the details and results of further testing will be presented.

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