

Heat treatment of codeposited aluminium–silicon coatings on ferritic steels by CVD-FBR technology

J.M. Brossard, M.P. Hierro, J.A. Trilleros, M.C. Carpintero, L. Sánchez, F.J. Bolívar, F.J. Pérez *

Universidad Complutense de Madrid, Dpto CC, Materiales e Ingeniería Metalúrgica, Avenida Complutense s/n, Facultad de Ciencias Químicas, 28040 Madrid, Spain

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Abstract

Ferritic steels are often used in boiler or supercritical steam turbines which operate at temperatures between 600–650 °C under pressure. Nowadays generation energy industries are interested in increasing the efficiency of the turbines. Increase of the operation temperature should meet this objective. In this study Al/Si protective coatings are developed by CVD-FBR at moderate temperature to respect substrates mechanical properties. Al–Si codeposition had been formed on three ferritic steels (P-91, P-92 and HCM-12 A). The initial parameters of the process were optimized by thermodynamic calculations using Thermo-Calc software. Then, those parameters were used in the experiments to obtain Al–Si coatings at low temperature and atmospheric pressure. Fe–Al intermetallic coatings containing Cr and Si were obtained. The effect of diffusion heat treatment was studied in order to allow the phase transformation from Fe₂Al₅ (brittle phase) to lower Al content phases such as FeAl (more fracture toughness).

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1. Introduction

Research in high temperature materials science including the study of corrosion and protection behaviour of materials in aggressive environments is widely stimulated by the aim to increase efficiency of clean electric-power generation plants [1,2]. An increase of steam temperature (from 580 °C to 630 °C or 700 °C) and/or the use of biomass or waste as fuel is expected to reach this goal with a reduction in the costs of energy conversion as well as to pollutants gas emission (CO₂, SO_x, NO_x). However the key problem which has to be considerate is to design suitable materials for boilers components such as heat exchangers that are resistant to creep, gas corrosion and hot corrosion at the operating temperature [3–5].

Although, austenitic steels and nickel-based superalloys [6–8] appear as attractive materials for their corrosion resistance, ferritic–martensitic steels are preferable due to their low thermal-expansion coefficients, higher low-cycle fatigue resistances, high-

er thermal conductivities and lower costs. Recently modified ferritic–martensitic steels 9% Cr steels (P-91, P-92) and 12% Cr (HCM12-A) are interesting candidates with adequate creep strengths up to possibly 630 °C. Addition of suitable coating containing Al and/or Si for example can increase corrosion resistance of these materials to temperatures up to their mechanical property limits. Diffusion coating containing a sufficient amount of Al and Si capable of developing a protective scale in conditions oxidation are particularly interesting [9–11]. Nevertheless temperature treatment of the selected coating process has to be below temperature of martensite transformation (700 °C [12]) in order to conserve mechanical properties of base materials. To achieve this goal, Chemical Vapour Deposition in Fluidized Bed Reactor (CVD-FBR) is particularly interesting because diffusion coatings can be obtained at relatively low temperatures ($T < 700$ °C) [13] and it has already been demonstrated to be an effective method to develop Al–Si coatings on AISI 304 [14].

The aim of this paper is firstly to develop and characterize Al–Si diffusion coatings obtained from Al and Si powder in fluidised reactor using H₂/HCl mixing gas as activator. Thermodynamics calculation were performed and used as guideline

* Corresponding author. Tel.: +34 91 39 44215; fax: +34 91 39 33457.

E-mail address: fjperez@quim.ucm.es (F.J. Pérez).

Table 1
Ferritic steels composition

wt.%	Fe	Si	Cr	Ni	Mn	Mo	W	Cu	other
HCM12	83.5	0.25	12.5	0.34	0.54	0.36	1.9	0.89	Nb,C,Al,V,N,Co,
P-91	89.3	0.40	8.1	0.38	0.50	0.92	–	–	P ₂ O ₅ (wt.%<0.4)
P-92	87.7	0.02	9.07	0.06	0.47	0.46	1.78	–	

to optimise CVD condition to perform Al and Si codeposition at moderate temperature. Then, the effect of heat treatment on diffusion coatings composition and structure was studied.

2. Experimental

2.1. Target materials

Composition of the three different ferritic steels used as base materials for Al–Si diffusion coating is presented in Table 1. The samples (10 mm × 10 mm × ξ with $1.5 < \xi < 2.5$) were polished from 240-grit SiC paper up to 600-grit SiC paper and then ultrasonically cleaned in alcohol, dried and weighed prior to coating experiment.

2.2. Coatings procedure

2.2.1. Thermodynamic calculation

Thermodynamic study of phase equilibrium (composition, partial pressure) during CVD were performed using Thermo-Calc computer program to determine the feasibility of metal deposition and provide a useful guideline to optimise deposition condition. Calculations are based on the free Gibbs energy minimisation code and mass conversion rule. SSUB3 and SOL2 databases (Scientific Group Thermodata Europe) were used to define chloride precursors and substrate respectively.

2.2.2. Experimental conditions

The fluidized bed reactor characteristics used in this study have been presented in previous works [15]. The bed was composed of powder mixture of Al (99.5% purity, grain size 200 μm)–silicon (97.5% purity, grain size about 40 μm) as metallic donor. Bed particles were fluidized using an important Ar flow (1.6 L min^{-1}). Al- and Si-chloride precursors were generated at coating temperatures by reaction between metallic donor powder and an input gas mixture 2.4 vol.% HCl and 28 vol.% H₂. Coatings were obtained using a two temperature steps procedure at 550 °C and 490 °C for 1 h and 30 min respectively. Some of the coated samples were heat-treated in a vertical furnace at 700 °C for 2 h under the inert gas Ar at atmospheric pressure.

2.3. Characterisation techniques

As deposited and thermally treated coatings were characterised by optical microscopy (OM), scanning electron microscopy (SEM JEOL JM-6400) and energy dispersive X-ray spectroscopy (EDS). Standard metallographic preparation was performed on samples prior to cross section observations. X-ray diffraction analysis (Philips X'PERT MPD, $K\alpha_{\text{Cu}}$ radiation)

Table 2

Equilibrium partial pressure of main Al- and Si-precursors formed for a fixed input ratio $\Phi^?(H_2)/\Phi^?(HCl)=12$

PP > 10 ⁻⁸	490 °C		550 °C	
	No substance	With, P-91, P-92, HCM-12	No substance	With, P-91, P-92, HCM-12
Ar	0.769	0.769	0.769	0.769
H ₂	0.226	0.226	0.225	0.225
HCL	1.72E-7	1.73E-7	5.64E-7	5.64E-7
AlCl ₃	0.00544	0.00542	0.00578	0.00578
AlCl	5.3E-6	5.2E-6	2.7E-5	2.7E-5
AlCl ₂ H	4.35E-5	4.30E-5	6.8E-5	6.8E-5
AlCl ₂	8.65E-9	8.62E-9	4.81E-8	4.81E-8
Al ₂ Cl ₆	2.52E-4	2.53E-4	7.27E-5	7.27E-5
SiH ₃ Cl	1.8E-5	1.81E-5	1.59E-5	1.59E-5

Input conditions: W(Al)=10 g, W(Si)=7 g, Ar : H₂ : HCl= 76.6:21.6:1.8 (vol.%).

were carried out to identify the phase composition of the coated sample and phases formed after diffusion treatment.

3. Results

3.1. Thermodynamics approximation

Thermodynamic calculations were performed for system Al_(s)/Si_(s)/Ar/HCl/H₂. Fe, Cr, Mn, W and Cu was also included in the system to consider the interaction between gas phase and BCC substrate.(Table 1). Input conditions used for calculation was guided by previous experimental studies [14,15]. Between 400 °C and 600 °C, the main Al- and Si-chlorides precursors (partial pressure > 10⁻⁸ atm) obtained from this calculation are Al₂Cl₆, AlCl₃, AlCl, AlCl₂, AlCl₂H, SiH₃Cl. The partial pressures of the main Al and Si precursors determined at 490 °C and 550 °C are presented in Table 2. AlCl₃ precursor is the main and the most stable chloride precursor present in all the temperature range studied whereas Al₂Cl₆ partial pressure decreases with temperature. SiH₃Cl partial pressure starts to decrease below the AlCl one around 540 °C, but is higher at lower temperatures (two times higher at 490 °C). We note that when BCC substrate is taking into account for calculations, no drastic effect is observed on the partial pressure of Al- and Si-chloride precursors. Nevertheless, new gaseous species from these calculations appear (Table 3) to indicate to substrate attack by the gaseous atmosphere. Partial pressures of these species are relatively low and are assumed to no perturb Al–Si deposition.

Table 3

Equilibrium partial pressure of main base materials gas formed for a fixed input ratio $\Phi^?(H_2)/\Phi^?(HCl)=12$

	490 °C			550 °C		
	HCM-12	P-92	P-91	HCM-12	P-92	P-91
MnCl ₂	4.7E-7	4.7E-7	5.29E-7	2.75E-6	2.71E-6	3.03E-6
MnH	1.33E-8	1.33E-8	1.5E-8	1.65E-7	1.63E-7	1.82E-7
MnCl	4.5E-9	4.5E-9	5.07E-9	1.4E-8	6.3E-8	7.05E-8
Mn ₂ Cl ₄	1.12E-9	1.12E-9	1.42E-9	5.42E-9	5.25E-9	6.58E-9
CuCl	5.2E-11	/	/	9.32E-10	/	/

Input conditions: W(Al)=10 g, W(Si)=7 g, Ar:H₂:HCl=76.6:21.6:1.8 (vol.%).

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