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Low cost rare earth elements deposition method for enhancing the oxidation resistance at high temperature of Cr_2O_3 and Al_2O_3 forming alloys

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Abstract

In this work a deposition method for coating Cr_2O_3 and Al_2O_3 forming alloys with rare earth elements is described. This is a modified CVD deposition method based on the pyrolysis of an aerosol produced by ultrasonic waves focused on the surface of a solution containing a soluble salt of the desired element that will later transform to oxide. To test the efficiency of the deposition method, commercial AISI-304 stainless steel samples were coated with lanthanum and cerium nitrates. Oxidation experiments have been performed in a thermobalance at 1173 K in synthetic air atmosphere for 25 h. Oxidation kinetics of coated samples was compared with that of an untreated one. Results show that samples coated with La and Ce improve their high temperature oxidation resistance by decreasing their parabolic rate constant of one order of magnitude. During the oxidation treatment $LaCrO_3$ perovskite forms in the scale of La-coated specimens while CeO_2 is the crystalline phase detected in the Ce-coated ones.

Keywords: Pyrolysis; Reactive metal effect; Stainless steel; High temperature oxidation

1. Introduction

Surface coating is an attractive way of overcoming industrial problems associated with microalloying reactive elements. The number of procedures described in the literature covers the whole set of known surface coating processes, but most of the work has been carried out on model binary or ternary alloys [1–16]. However, most of the processes described results either in non-homogeneous coatings or are costly enough for preventing industrial applications.

In this work we describe the setting up of a modified CVD procedure, firstly described by Spitz and Viguie [17] for obtaining monodispersed powders, that results in surface deposition of lanthanum and cerium salts that enhances the resistance to high temperature oxidation of AISI-304 grade stainless steels up to 1173 K.

2. Experimental

Coupon specimens of commercial AISI-304 stainless steel samples (ACERINOX S.A.) 10×20×1 mm were used.

X-ray diffraction experiments (XRD) were performed in a Siemens Krystallograph D-5000 instrument, using CuKα radiation and pyrolytic graphite as monochromator. A JEOL JS-400 instrument was employed for scanning electron microscopy experiments equipped with an EDX spectrometer (OXFORD LINK PENTAFET E-6587). Isothermal oxidation experiments were carried out in a SETARAM TG-DTA 92 thermobalance under synthetic air at 1173 K during periods ranging from 2 min up to 25 h.

Lanthanum and cerium deposition was carried out by pyrolysis of a salt-containing aerosol [18,19] using an ultrasonic generator RBI 79-01. The system has a piezoelectric generator of ultrasonic waves placed in the base of the solution container. The geometry of the system allows the wave focusing over the solution surface. Frequency and vibration intensity can be regulated by the generator so that the aerosol particle size is controlled within a narrow band to obtain an optimum size [20].

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The aerosol is carried out by a nitrogen flow so that in the furnace the solvent is vaporised liberating the salt and depositing numerous microdroplets on the steel surface. The process can be considered as a modified Chemical Vapour Deposition (CVD) [21].

3. Results and discussion

Deposition process, described above, can be controlled by acting on parameters affecting aerosol generation, dissolution density and surface tension and the interaction between substrate and deposited salt. Optimum values for all other parameters are determined by varying them in a wide range while, at the same time, keeping in mind that scaling up of the process should consider total costs. The parameters acting on aerosol generation (frequency and intensity) are kept constant.

Acetone, methanol and deionised water are used as solvents covering a reasonable range of dipolar moments and dielectric constants.

Solution concentration may determine the diameter of deposited microdroplets, of which two were tested: 0.05 and 0.1 M. Solutes used in this work are soluble salts leading oxides by thermal treatment and it is also required that decomposition of the salt results in products that do no affect the steel substrate. Thus, chlorine and sulphur containing salts that might adversely affect the alloy at high temperatures should be avoided. For these reasons lanthanum and cerium nitrate hexahydrate were used.

Finally, the interaction between the deposited salt and the metallic substrate is modified on changing the carrier gas and the interaction temperature. There are two reasons leading to the election of nitrogen as carrier gas. First, scaling up: if the process is to be envisaged as of potential interest the cost is a determinant factor. Second, election of a reactive atmosphere, like synthetic air, might result in oxidation effects that could increase difficulty of interpretation of data. Besides this, this process should take into account that the residence time of the aerosol particles in the reaction area is small in order to avoid secondary reactions and the furnace temperature must be high enough to evaporate the solvent allowing direct contact between the salt and alloy surface. These conditions open a range of gas flow from 1 to 6 l min^{-1} and temperatures from 373 to 623 K.

Once all the above variables are fixed, the interaction time determines the amount of lanthanum-containing salt deposited onto the stainless steel surface. The interaction time range depends upon the quantity of material necessary to produce the REE. Previous results have shown that 0.1 wt.%, or even less, of reactive element is enough to produce such effect and higher quantities will not improve the behaviour of the stainless steel [22]. Based on these considerations, deposition time was varied between 2 and 15 min.

Table 1
Optimum parameters for lanthanum and cerium deposition

	Range of values	Selected parameters
Solvent	Methanol or Deionised water	Deionised water
Concentration	0.1 M	0.1 M
Carrier gas	N_2 at 3–5 l min^{-1}	N_2 at 3 l min^{-1}
Temperature	473–523 K	473 K
Deposition time	10–15 min	10 min

As a result of all the observations, the optimum range of experimental parameters is shown in Table 1 together with the finally selected values.

After the deposition procedure the presence of numerous spherical particles of variable diameter covering the steel surface are observed. The particle size distribution has been estimated from a total number of 1143 particles for La-deposited and 381 for Ce-deposited specimens. The average particle diameter is 0.76 μm and 0.90 μm for La and Ce coated samples respectively, Fig. 1.

Ion implantation doses of about 10^{16} atoms cm^{-2} are demonstrated to produce the REE [23]. In the same way, it is admitted that a reactive element concentration of 1 wt.%, or even less, are enough to produce this effect [22]. Taking into account the average particle size deposited and the number of particles observed it is possible to calculate the number of lanthanum atoms per square centimeter if we know the density of the deposited particles. Assuming that the spheres are dense La_2O_3 particles we can estimate

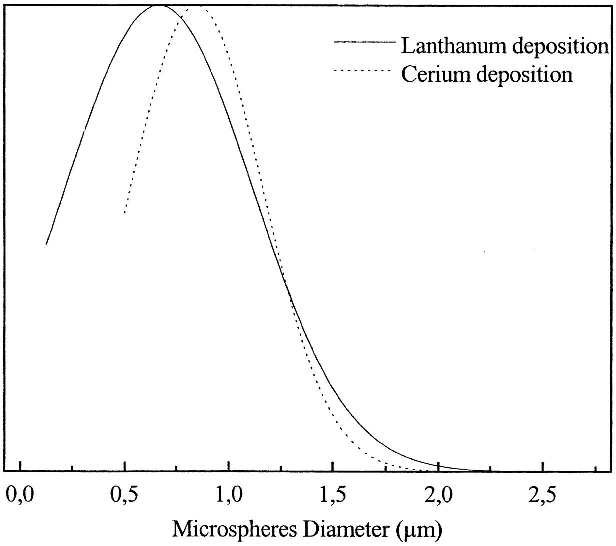

Fig. 1. Microspheres diameter distribution for La and Ce coated samples by PYROSOL method.

a lanthanum coverage of around 4×10^{16} La^{3+} ions cm^{-2} which is in the same order of magnitude that usual implantation doses specimens [23].

Oxidation under synthetic air at 1173 K shows that both lanthanum- and cerium-deposited samples show parabolic kinetics indicating a protective behaviour of the oxide scale whereas the untreated specimen present a pseudo-parabolic behaviour up to 10 h. This behaviour is sharply modified for longer times, increasing dramatically the mass gain after 10 h oxidation at 1173 K, which clearly indicates a non-protective behaviour of the oxide scale in the case of the untreated sample. Total mass gain is presented in Table 2. Monitoring the weight change during the cooling cycle, spallation phenomena is clearly observed in the untreated sample while for the lanthanum and cerium treated samples spallation is completely absent within the precision of the thermogravimetric device.

From the total mass gain by surface unit, an estimate of the oxide layer thickness can be calculated. Assuming that the scale is formed only by M_2O_3 type oxides (M=Fe, Cr) an average density for a compact oxide scale of 5.2 g cm^{-3} is supposed as a good approximation. Then, the scale thickness can be calculated through the expression: $t(\mu m) = 6.4\Delta W(mg\ cm^{-2})$.

This value will underestimate the actual scale thickness since scale porosity will result in densities below the theoretical one.

Thermogravimetric data are usually explained in base of the Wagner's law [24]. However, oxidation process may follow different kinetics. We propose, according to Baxter and Norton [25], that the total mass gain vs. time curve is the result of the convolution of more than one process. Assuming that, together with the parabolic behaviour described in Wagner's law, a linear term is present accounting for direct contact of the gas phase with the metal, the following expression can be written:

$$\Delta W = k_l t + k_p t^{1/2} + \Delta W_0$$

where k_l and k_p are the linear and parabolic constants respectively and ΔW_0 a constant that accounts for the errors in the initial mass weight. Fitting of the experimental curve results in the constants shown in Table 2. These results show that lanthanum is more effective in reducing the oxidation rate of the steel, both linear and parabolic rate constants being lower than for Ce-deposited specimens. Nevertheless, the presence of a linear term may suggest that the deposition treatment results in the formation of small blisters, even in the selected working conditions that accounts for it in the kinetic law.

XRD results are shown in Fig. 2. Species formed differ from one specimen to another. The scale developed on the La-deposited specimen is enriched in Fe. XRD patterns for this sample shows the formation of Fe_2O_3 and and $Mn_{1+x}M_{2-x}O_4$. The only metallic phase detected in this sample is austenite. The oxide phase associated with the rare earth in this sample is $LaCrO_3$ perovskite. Contrary to this sample, in the Ce-deposited specimen the scale is mainly formed by Cr_2O_3 and $Mn_{(1-x)}Cr_{(2-x)}O_4$ indicating the Ce is more effective in enhancing the Cr diffusion towards the scale. No austenite is detected but a very intense martensite peak can be seen in the XRD pattern due to the formation of martensite near the scale-to-alloy interface by chromium migration to the scale. This leaves the alloy enriched in Fe and Ni and thus forming martensite on cooling to room temperature.

4. Conclusions

The lanthanum deposition method developed in this work using pyrolysis of aerosols proves to be a very efficient low cost way of increasing the high temperature oxidation resistance of conventional stainless steels. Parabolic rate constant values show that the scale rate formation is reduced by one order of magnitude when samples are deposited with reactive elements with this method.

This method can be extended to other Cr_2O_3 and Al_2O_3 forming alloys and the use of soluble salts of other reactive elements.

The variables that control the deposition method are such that can be easily scaled from laboratory to industrial processes.

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Table 2
Total mass gain and equivalent thickness for untreated and La- and Ce-deposited AISI-304 stainless steel after 22 h oxidation at 1173 K

Sample	Mass gain (mg/cm^2)	Thickness (μm)	k_p ($mg\ cm^{-2}\ h^{-1/2}$)	k_l ($mg\ cm^{-2}\ h^{-1}$)
Untreated	4.36	27.9	–	–
Ce-deposited	0.48	3.07	0.06841	0.00556
La-deposited	0.20	1.27	0.02241	0.00104

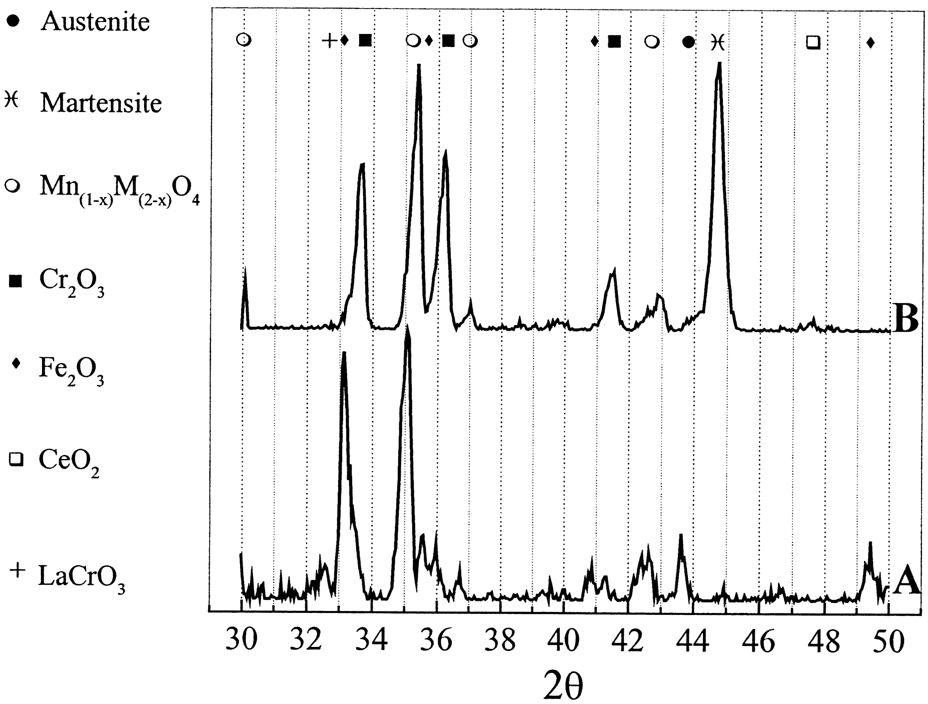

Fig. 2. XRD pattern of La-deposited (A) and Ce-deposited (B) after 22 h oxidation at 1173 K.

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