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Oxidation behviour of sol-gel zirconia coated 9Cr-1Mo ferritic steel in air atmosphere

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The oxidation behaviour of sol-gel derived zirconia coated 9Cr-1Mo ferritic steel has been examined at 700-900°C in air atmosphere. X-ray elemental mapping of the coated surface detected a continuous band of zirconium and oxygen, attributing to the presence of zirconia coating of around 2 µm in thickness. Oxidation kinetics indicates that the oxidation rate constant of the coated substrates decreases an order of magnitude lower as compared to uncoated substrates. Measurement of a noticeable increase in activation energy of the coated surface is further evidence towards the improvement of the oxidation resistance of the steel after coating development. Microstructural examination through field emission scanning microscope (FE-SEM) of the oxidized substrates show the presence of comparatively thin, less porous and compact scale at the coated surface than uncoated surface.

Keywords: Sol-gel zirconia coating, Cr1Mo ferritic steel, Oxidation kinetics, Oxygen atmosphere

9Cr-1Mo steels, particularly ferritic, are widely used in high temperature applications like petrochemical industry, power plants, etc. Their superior properties like higher mechanical strength, creep resistance, weldibility, lower thermal expansion coefficient etc make them useful structure material for high temperature applications, In addition, this grade of ferritic steel is less costly and easily machinable. At high temperature, Cr bearing steels form a protective chromium oxide which increases their oxidation resistance till it remains adherent to the metallic substrate[1-5]. At particular temperature, the adherence of chromium oxide film start to decrease that results spallation and the cracking of oxide layer. This ultimately decreases the interfacial Cr content and subsequently enhance the oxidation of iron[2,5]. Earlier several efforts were made in the improving the oxidation resistance of Cr bearing steels by developing oxidation resistance ceramics coating using different techniques likes physical-vapour deposition (PVD), pack cementation, chemical-vapour deposition (CVD)etc[6-11]. One of the draw backs with these techniques is that they need high temperature and pressure conditions in the development of coatings. The quality of the coating is also not good because of the presence of porosities.

On the other side ceramics coating like Al_2O_3, ZrO_2, SiO_2, SiO_2-TiO_2 etc. developed through sol-gel process proven their better effectiveness in improving the oxidation resistance of metallic materials[12-16]. Among them, zirconia coating is preferred due to their superior hardness, low thermal conductivity, good mechanical and chemical durability at high temperature. The thermal expansion coefficient of zirconia matches with many of the metals that control the rupture or cracking of the coating. This is the another advantages of developing zirconia coatings in order to control spallation/ cracking of the scale.

Li and co-workers[17] developed sol-gel zirconia coating using zirconium-n-propoxide as a precursor material to prevent the oxidation of the steel. Apart from this, several studies have been carried out on the corrosion protection of stainless steel by sol-gel zirconia coatings[18-22]. Structural and optical properties of the sol-gel zirconia coatings developed on glass substrate were studied by Ehrhart *et.al.*[23]. In a novel approach, nano structured sol-gel zirconia coatings were developed on aluminum, stainless steel and glass substrate through PROSOL process[24]. Recently, an excellent hot corrosion resistances of sol-gel zirconia coated 9Cr-1Mo ferritic steel in molten LiCl-NaCl and Na_2SO_4-K_2SO_4 systems was observed [25]. In the present work we report the oxidation behavior of nano structured zirconia coated 9Cr-1Mo ferritic steel at 700-900°C temperature range in air atmosphere.

Experimental Section

Synthesis of zirconia sol

Zirconia oxy hydroxide [Zr O(OH)] sol was prepared by hydrolysis of zirconium (IV) propoxide in organic solvent in the presence of water. In the preparation of sol, zirconium (IV) propoxide and *n*-propanol were mixed together in their 1:10 ratio. Acetyl acetone was added in the mixture along with addition of few drops of water while continuous stirring of the mixture solution. The mixed solution was stirred up to 4 h with continuous stirring. Once the solution became miscible, the stirring was stopped as the resultant solution oxy hydroxide of zirconium was formed and found to be stable. The details of the synthesis of zirconia sol are available elsewhere[25].

Coatings development

The test specimens (dimension = 30 mm × 15mm × 3mm) were cut from the 9 Cr-1Mo ferritic steel (Cr = 9%, Mo = 1%, C = 0.11%, V = 0.13%, Nb = 0.09%, Mn = 0.48%, Si = 0.3%, S = 0.005% , P = 0.018%, N = 0.051%, Al = 0.015%, Co = 0.015%, Cu = 0.05% and rest is Fe) sheet of thickness 3mm for oxidation and microstructural studies. The cut specimens were metallographically polished by grinding them with various grades of emery paper followed by mirror polish with alumina (size 3 µm) suspension. The polished specimens were thoroughly degreased with acetone. Further, the degreased specimens were dipped in hot (60°C) nitric acid solution (10 volume %) for proper roughening of the surface. Roughening of the surface is necessary to obtain better adherence of coating while applying sol-gel process of coating development. Afterwards, the synthesized zirconia sol was coated on the prepared specimen through dip coating technique with a constant withdrawal speed of 1 cm/sec (approx). The coated specimens were dried in air for 10 min. The air dried coated specimens were heated at 300°C for half an hour. Then, specimens were again heated at 600°C for one hour for complete sintering of the coatings.

Surface topography and microstructural examination

Cross sectional analysis of the oxidized specimens was examined after cutting it carefully with the help of high precision diamond cutting wheel in the presence of a coolant. VEECO make Nano Scope AFM was employed for measuring the particle size of the sol-gel coatings and surface roughness of the coated surface. Elemental X-ray mapping through the cross section of the coated specimen was done using an FEI-made field emission-scanning electron microscope (FE-SEM) attached with an EDS system. Cross sectional morphology of the oxidized coated and uncoated specimens was examined using Scanning electron microscopy (Jeol, JSM 5600).

Oxidation kinetics

The oxidation kinetics of the coated and uncoated specimens was carried out at 700, 800, 850 and 900°C in a muffle furnace using weight loss measurement. The weight gain of the test specimens was measured after regular intervals of time using a Mettler balance. The kinetic equation used for the elucidation of rate constant is given as

$$(\Delta W/A)^2 + C = Kt \qquad \ldots (1)$$

where $(\Delta W/A)^2$ is square of weight gain per unit area, t is the time and K is rate constant.

The value of K was measured by dividing the square of weight gain by exposure period. The measured values of rate constant were expressed in mg^2/cm^4 min. Arhenius equation used for the determination of the activation energy, is given as

$$K = Ae^{-Ea/RT} \qquad \ldots (2)$$

where, E_a is the activation energy, R is gas constant and T is temperature.

Results and Discussion

AFM and EDS analysis of the coated surface

Figure 1 depicts the AFM micrographs of the sol-gel zirconia coated substrates. The AFM micrograph reveals the roughness of the surface which covered by zirconia particles. Because of the uneven surface of the substrate, the coating present in the grooves (dark areas) is not clearly visible in the micrographs. The average size of the zirconia particles was determined as 13-15 nm in size[25]. Elemental X-ray mapping of the coating through its cross section as shown in Fig. 2, demonstrate the presence of a continuous band of oxygen and zirconium alongwith base elements chromium and iron. Identification of Zr in the coated layer confirmed the successful development of

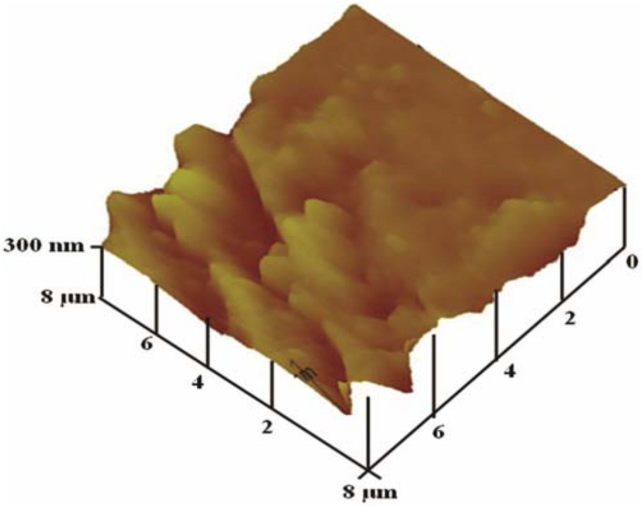

Fig. 1 — AFM micrograph of zirconia coated 9Cr-1Mo steel specimen showing roughness of the surface.

zirconia coating. The thickness of the coating appears to be quite thin (~2 µm). Presence of Zr along with iron in the coating suggests their involvement in making Fe-Zr phase. XRD analysis has also evidenced the presence (Zr_6Fe_3O)Fe phases just beneath the coating[25].

Oxidation kinetics

The square of weight gain versus time plots for the uncoated and coated specimens oxidized at 700, 800 and 900°C in air atmosphere for 24 h, are shown in Figs 3 and 4, respectively. Oxidation trend of the uncoated specimen show a parabolic behavior at 700 and 800°C. At 900°C, their oxidation kinetics appears to become quite fast. The original oxide film consisting of chromium rich iron oxide (Fe, $Cr)_3O_4$ and iron oxide (Fe_3O_4)[15] present at the surface of the substarte, able to control the oxidation reaction up to maximum level till 800°C. At 900°C, the cracking of scale starts supposedly that make channel for the diffusion of oxidized metal ion from the bulk metal towards outer scale. At the same time inward diffusion of oxide ions towards the inner oxide scale occurs that results in the enhancement of oxidation reactions. The enhanced oxidation reaction results the thickening of scale which likely becomes porous with time. At this stage, the diffusion of oxidized metal ion and oxide ion may occur without any hindrances[18].

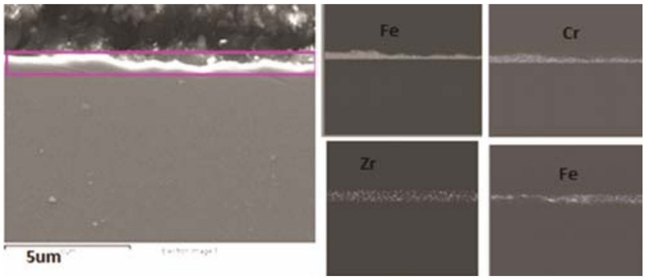

Fig. 2 — Elemental x-ray mapping of Fe, Cr, Zr and O through the coated layer.

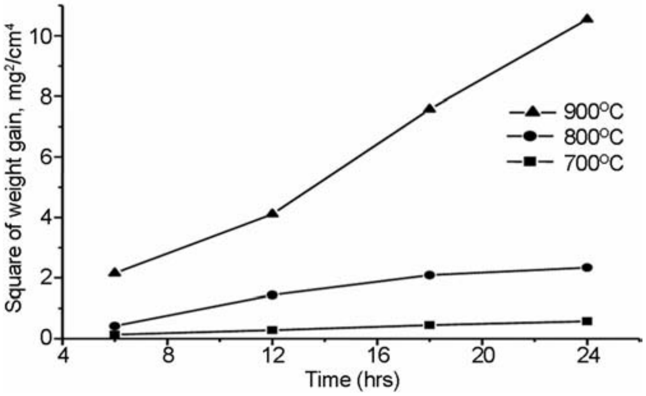

Fig. 3 — Square of weight gain vs time curves for the uncoated 9Cr-1Mo steel specimens oxidized at 700, 800 and 900°C for 24 h.

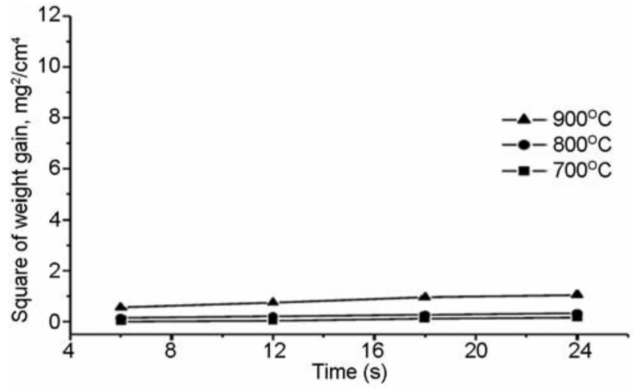

Fig. 4 — Square of weight gain vs time curves for the coated 9Cr-1Mo steel specimens oxidized at 700, 800 and 900°C for 24 h.

As compared to uncoated substrate, the oxidation kinetics of the coated substrates seems to occur at very slow rate up to 800°C. At 900°C, an increase of weight gain was also noted for the coated substrates. Though, the comparative increase in weight gain of the coated substrates occurred very less than uncoated substrates. Presence of zirconia coating makes (Zr_6Fe_3O)Fe phases over the surface[25] that able control oxidation reaction up to 800°C. The oxidation rate constants (mg^2/cm^4 min) derived from the Eqn.1, are given in Table 1. From the oxidation rate data, it can be noted that rate constant for the coated specimen occurs an order of magnitude lower than that of the uncoated specimen. Activation energies derived for the coated and uncoated specimen (Fig. 5, Table 2) indicates their noticeable decrease at the uncoated specimens as compared to the coated specimens. Based on the oxidation kinetics, it can be concluded that the sol-gel derived zirconia coating makes a substantial improvement in the oxidation resistance of the studied 9Cr-1Mo steel in air atmosphere.

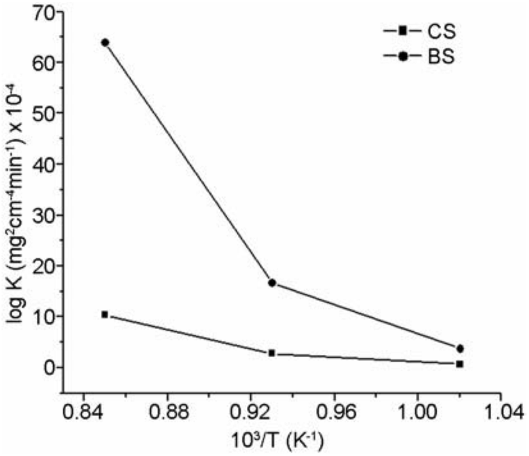

Fig. 5 — Arrhenius plots for coated (CS) and uncoated (BS) surfaces

Microstructural examinations

Figures 6 and 7 depict the cross-sectional views of the uncoated and coated specimens oxidized at 700, 800°C and 900°C, respectively. The morphologies of the uncoated oxidized specimens exhibit the presence of a thick and porous scale. The thickness of the scale increases with the increase of temperature as around 20 µm thick scale forms at 700°C (Fig. 6a) which become more than 45 µm at 800°C (Fig. 6b). Scale also becomes in multilayered structure. The exact thickness of the scale formed at 900°C could not be estimated for the uncoated specimens due to start of spallation (Fig. 6c). On the other side the cross cross-sectional view of the coated specimen oxidized at 700°C showed the presence of a thin and compact oxide scale (thickness ~ 5µm) (Fig. 7a). The thickness of the oxide scale became nearly 10 µm at 800°C (Fig. 7b). This indicates that slow oxidation reaction make more compact oxide scale at the coated specimens. However, the oxide scale formed at 900°C is appeared to be less compact and porous structures (Fig. 7c). An increase in the oxidation rate of the coated specimen at 900°C is due to the occurrence of a fast diffusion phenomena through the metal/scale interfaces. However, oxidation reaction occurs quite slow at 900°C at the coated surface as compared to uncoated surfaces (Tables 1 and 2).

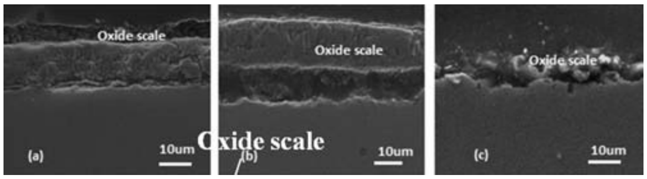

Fig. 6 — Cross-sectional views of uncoated 9Cr-1Mo steel specimens oxidized at 700°C (a), 800°C (b) and 900°C (c) for 24 h.

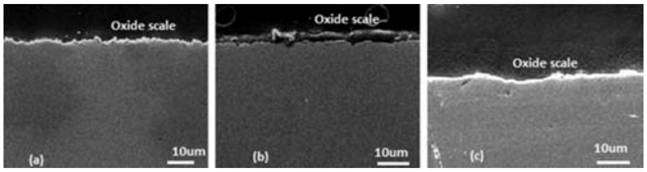

Fig. 7 — Cross-sectional views of zirconia coated 9Cr-1Mo steel specimens oxidized at 700°C (a), 800°C (b) and 900°C (c) for 24 h.

Table 1 — Oxidation rate constant measured for zirconia coated and uncoated 9Cr-1Mo steel

Substrate (9Cr-1Mo steel)	Oxidation Rate constant, K (mg^2/cm^4 min)		
	700°C	800°C	900°C
Coated	6.9×10^{-5}	2.8×10^{-4}	1.1×10^{-3}
Uncoated	3.74×10^{-4}	1.6×10^{-3}	0.64×10^{-2}

Table 2 — Activation energy measured for zirconia coated and uncoated 9Cr-1Mo steel

Substrate (9Cr-1Mo steel)	Activation energy, Ea (KJ/mole)		
	700°C	800°C	900°C
Coated	16.619	14.715	12.686
Uncoated	12.02	9.66	8.272

Conclusions

i) The sol gel synthesized zirconia coating is found quite effective in improving the oxidation resistances of 9Cr 1Mo ferritic steel up to 800°C. At 900°C, the oxidation resistances of the coated substrates start to decrease in a noticeable rate.

ii) Oxidation kinetics indicate an order of magnitude lower oxidation rate for the coated substrates as compared to uncoated substrates.

iii) Measured activation energy indicates their decrease for the coated substrates.

iii) Microstrucural examination of the oxidized specimens suggest a thin, compact and cracks free scale forms at the coated surface whereas a thick, multilayered and porous scale forms at the uncoated surface.

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