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High Temperature Oxidation Studies of Nanostructured Cr/Al Multilayer Coatings on Superalloy

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Abstract—*The cyclic high temperature oxidation of sputtered Cr/Al multilayer coatings deposited by DC magnetron sputtering on the superalloy substrate has been studied in the present work. The structural features of the coatings were characterized by FE-SEM and XRD. The weight change measurements were made to calculate the cyclic oxidation kinetics of the coatings, in air at 900°C. It was observed that the oxidation rate of sputtered Cr/Al multilayer coated superalloy is lower than that of the bare superalloy due to the formation of defects free scale i.e., continuous, dense, adherent and protective oxide scale over the surface of the coatings. The protective oxide scales are basically the thin layer of* Cr_2O_3 *and* Al_2O_3*, which has formed over the Cr/Al multilayer coated superalloy substrate exposed to air at temperature, 900°C.*

Keywords: *Cr/Al Multilayer coating, DC magnetron sputtering, High temperature Oxidation*

1. INTRODUCTION

Nanotructured multilayer coatings provides better oxidation resistance as compared to the bare superalloy[1-9]. Li. Tiapeng et al. [5] reported that multilayer CrAlN magnetron sputtered coatings on K38G alloy formed continuous alumina scale at 900⁰C, which in turns improved cyclic oxidation resistance. Chromium and aluminum are two important corrosion inhibitors which are used in coating for high temperature application in order to improve the efficiency and oxidation resistance of gas turbine for the longer period of use. Chromium forms protective Cr_2O_3 scale below 900°C, where as aluminum forms stable Al_2O_3 scale above 900⁰C, due to this reason, these two elements are used in coating for high temperature application, in order to improve the cyclic oxidation resistance of coated superalloy. Nanostructured coatings plays a great role in high temperature application because of : i) it provides continuous defects free scale on the surface, ii) requirements of inhibitor in coating is less as compared to microcrystalline coating[10]. Structural and chemical composition of the coated samples were determine by XRD and FE-SEM/EDS. Improved high temperature oxidation mechanism of coated samples are discussed.

2. SYNTHESIS OF THE FILM

Cr/Al multilayer coatings were deposited on superalloy substrate by DC magnetron sputtering process. Al and Cr (99.99 % pure) are used as a target material. Base pressure 3 X 10^{-6} Torr, Deposition gas pressure (Ar) 10 mTorr, Substrate Temperature 200° C & 300° C and total Deposition time 02 hrs were used for the deposition of the multilayer coatings on superni-718 substrate. It is worth to mention here that multilayer Cr/Al coating deposited above 300°C, were peeled off due to induced thermal stress in coating.

2.1 Thermogravimetrci study

High temperature oxidation studies were done in air. Sample was heated in muffle furnace at 900°C for 1 hr and then removed the sample from the furnace and cooled up to room temperature for 30 minute. The change in weight / area of the sample was recorded. This process was continued for 50 cycles. The change in weight/area versus cycles was plotted. The graph is used for calculation of the oxidation kinetics.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis of the coatings

Structural analysis of the coated and un coated samples are done by XRD and their results are shown in Fig. 1(a). The average grain size of the coated samples is determined by its XRD peak broadening according to Scherrer formula [11]. It was seen in the range of 20-70 nm. Only aluminum phase is present in all coatings because. XRD analysis confirmed that no chromium phase is present in coated sample. Similarly the XRD results for the oxidized samples are shown in Fig. 1(b). Cr_2O_3, NiO, Fe_2O_3 oxide scale were found on the bare superalloy when it is heated at 900°C and Cr_2O_3, Al_2O_3 and Fe_2O_3 oxide were seen in the oxidized coated samples.

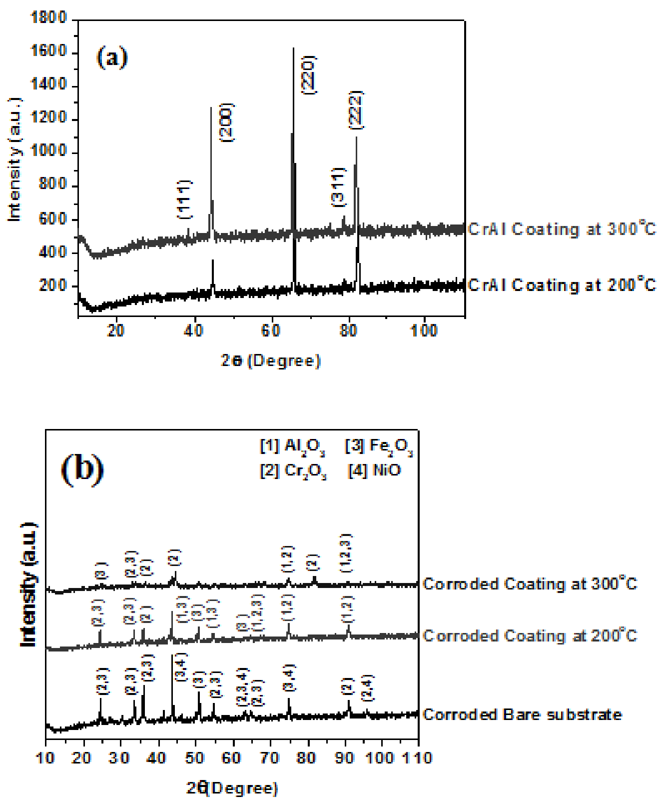


Figure 1: XRD results of (a) Coated sample and (b) oxidized bare and coated sample

Surface morphology with EDS results of coated sample at 200°C and at 300°C are presented in Fig. 2(a-b). V-shaped grains with dense morphology is seen in case coated sample at 200°C, where as elongated V- shaped grains is seen in case of coated sample at 300°C, it is due to zone 3 structures as reported in R.Meissier's work[12]. The thickness of coatings was approximately 11.3 µm and it was determined cross-sectional FE-SEM micrograph.

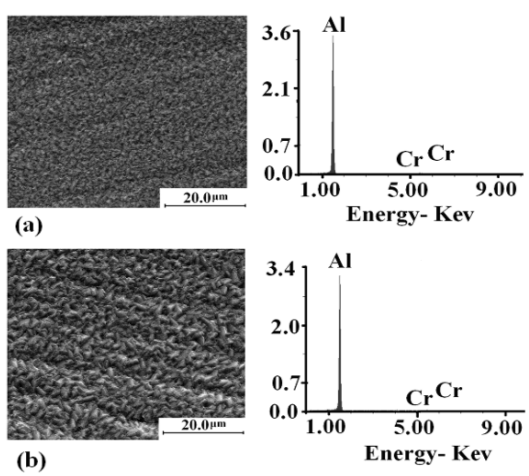


Figure 2: FE-SEM/EDS Surface micrographs of coated sample (a) at 200°C and (b) at 300°C

3.2 Oxidation Studies in Air environment

Bare substrate and coated samples are pushed into Muffle furnace and heated in air environment at 900°C for 50 cycles. The data of weight changes /area versus number of cycles are plotted for samples and is represented in Fig. 3 (a). It is seen that the bare substrate has poor oxidation resistance as compared to coated samples. After 25 cycles bare substrate shown higher weight gain due to defects in scale i.e. pores and spallation of scale.In case of coated sample overall weight changes /area is less**.** Coated sample at 300°C substrate temperature shows the least weight gain /area. The K_p value calculated from Fig. 3 (b). The calculated K_p value for the coated sample (at 200°C and 300^{0}C) on superalloy is found very less (0.3469 X 10^{-10} g^2 cm^{-4} s^{-1} and 0.01444X 10^{-10} g^2cm^{-4} s^{-1}) as compared to the K_p value of bare substrate (12.51 X 10^{-10} $g^2cm^{-4}s^{-1}$). Thus, coated sample at 300^0 C shown better oxidation resistant at 900^0 C in air environment.

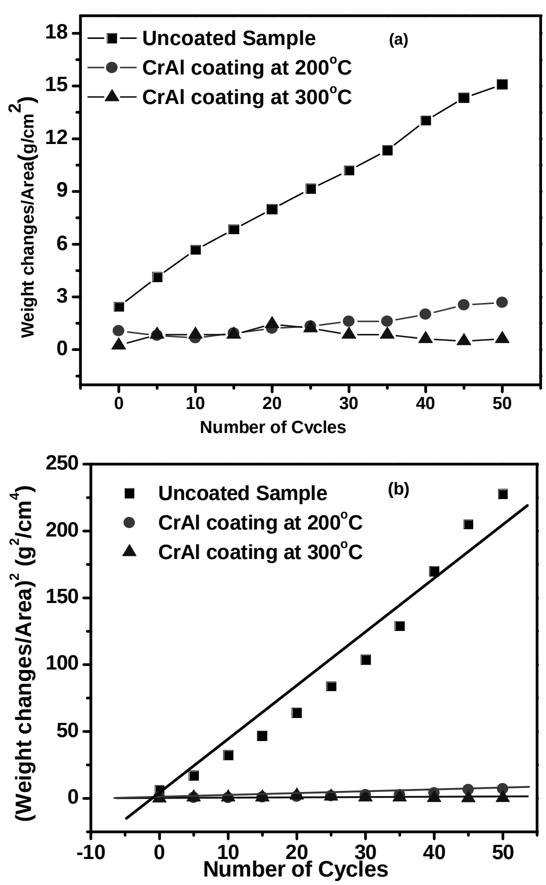


Figure 3 (a) Weight variation (g/cm^2) versus number of cycles and (b) K_p value for bare and coated samples oxidized in air at 900°C

3.3 Oxide products analysis

Fig 4 (a-d) represent the FE-SEM surface morphology of oxidized bare substrate. Oxide scale has defects like pores (Fig.4 (a)), cracks (Fig.4 (b)), and spallation (Fig.4 (b), 4(d) .

Fig 5 (a-b) indicate the surface micrographs of oxidized coated samples. Sample coated at 200^0C substrate temperature shows thin needle type morphology of oxide scale (Fig.5(a)) where as sample coated at 300^0C substrate temperature shows thick needle type morphology of oxide scale (Fig.5(b)). There are no defects in oxide scale in both coated sample as evident by FE-SEM surface morphology (Fig.5 (a-b)).The oxide scale Al_2O_3 and Cr_2O_3 are formed on the surface of the coating and it was confirmed by EDS analysis. FE-SEM surface analysis results revealed that both coated sample shows good oxidation resistance in air environment at 900^0C for 50 cycles. EDS results indicates that sample coated at 300^0C (Fig.5(b)) substrate temperature has high amount of alumina content (87.73 wt%) in scale as compared to sample coated at 200^0C (Fig.5(a)) substrate temperature(67.56 wt%) which is necessary for providing sufficient protection to the Superni-718 in the high temperature environment.

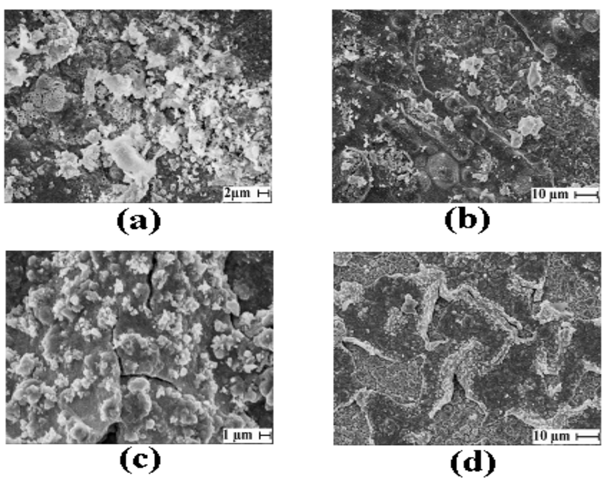
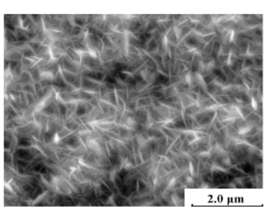
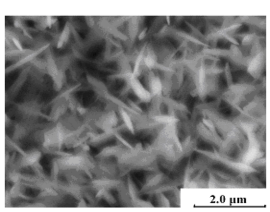


Figure 4 (a-d) Surface morphology of oxidized bare Substrate



Element	Wt %	Mol%
Al_2O_3	67.56	75.64
Cr_2O_3	32.44	24.36

(a)



Element	Wt %	Mol%
Al_2O_3	87.73	90.92
Cr_2O_3	12.26	09.08

(b)

Figure 5 (a-b) Surface morphology with EDS of oxidized coated sample at different substrate temperatures (a) at 200^oC and (b) at 300^oC

The objective of the designing of multilayer layer coating on superalloy substrate was that the top layer should be enriched with aluminum coating followed by chromium layer coating, so that outer layer forms stable aluminum rich oxide scale followed by chromium rich oxide scale, in order to increase the oxidation resistance of superalloy at 900^0C.

Coated sample at 300^oC has better oxidation resistance as compared to that of the coated sample at 200^oC substrate temperature due to : i) Coated sample was uniform with dense, ii) surface morphology of oxide scale was defects free which work as an oxidation barriers, and also iii) oxide scale has enriched alumina content. The results of lower oxidation rate of Nanotructured coated sample is in accordance with the results of X. Ren and F. Wang [13].

4. CONCLUSION

Magnetron sputtered Cr/Al multilayer coated sample at 200^0C and 300^0C was exposed in air at 900^0C in muffle furnace. The oxidation kinetics of coated samples were compared with that of the un coated sample . The K_p value of the coated sample is less due to the formation of defects free and protective oxide scale. The increased in weight continuously in case of un coated sample was due to defects in scale i.e. the spallation, cracks and pores. The XRD results revealed that Cr_2O_3, Al_2O_3 and Fe_2O_3 oxides are formed on the oxidized coated samples. Results of the surface morphology of oxidized coated sample shown that the oxides formed on the surface were defects free.

Coated sample at 300^oC, showed a lower K_p value. It might be due to the uniform morphology, smaller grains (20-40nm) of the coatings, and thick morphology of scales/oxides with higher amount of alumina (87.73 wt %)..

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