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Sindh Univ. Res. Jour. (Sci. Ser.) Vol.49(2) 393-398 (2017)

SINDH UNIVERSITY RESEARCH JOURNAL (SCIENCE SERIES)



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Received 3rd January 2016 and Revised 9th July 2016

Abstract: Ni based super alloys have been used for blades and vanes of the aeroengine hardware. The main purpose of these alloys is to provide the high temperature strength under aggressive environments. However, the alloying elements used donor yield the desired resistance against oxidation to the components. In order to provide optimum oxidation resistance and enhance engine working efficiency, a system of the coating is applied which is usually called thermal barrier coating or TBC system typically comprising of two films or layers i.e. ceramic one which is topcoat (TC) and an underlying metallic layer as a bond coat (BC). One of the crucial parts of the TBC system is the nickel aluminides (β NiAl) that are used as BC material. This research involves the preparation of the nickel aluminide coatings onto CMSX-4 superalloy using pack or in-situ chemical vapour deposition (CVD) method. Coating quality produced is dependent on the processing parameters or conditions consequently influencing the TBC lifetimes. Therefore, this research investigates the influence of (in-situ CVD) processing parameters i.e. Al contents, time, temperature, and activator contents on the β NiAl coatings. The coating characterisation was carried out by utilising field emission scanning electron microscope (FESEM) equipped with EDS and powder X-ray diffraction (XRD). The results demonstrated that all of these parameters affect the coating thickness and micro structural evolutions significantly except activator which has mild effect. In particular, coating time was observed to be more pronounced i.e. coating thickness was found to be increased proportionally as the time. The discussion is presented on the deposition mechanisms and micro structural features of the coatings.

Keywords; Nickel Aluminides, In-situ CVD, Activator, Time, Al and Coating Thickness.

2.

INTRODUCTION

Thermal barrier coatings (TBC) system is commonly employed onto aeroengine turbine blades in order to enhance engine efficiency and component lifetime (Clarke 2003). It consists of topcoat and bond coat (BC)and a layer called 'thermally grown oxide' (TGO). The most of TBC failures are because of BC except the mechanical ones. The most general form of the BC applied in the TBC is the β nickel aluminide based. The aluminide based BCs consist of an ordered B2 structure that has attracted considerable attention in last several decades owing to their high temperatures of melting, lower density, and tremendous resistance against oxidation (Sudhangshu 2011). There are several methods used to produce BNiAl coatings; for example in-situ CVD, out-of-pack and CVD etc. Among all, the cost effective method is in-situ CVD. The quality of coating depends on the processing parameters; e.g. (Zhenhua et al. 2014). (Xu, et al. 2015) examined the effect of processing parameters on micro structural evolution of the coating by using CVD method. They concluded significant effect on micro structural development of the coating upon the variation of processing conditions. In contrast, this investigation is to create an understanding of the processing conditions causing the micro structural variations. The coating thickness (CT) is of prime importance, because, the higher it is, the greater is the Al reservoir required for optimum oxidation. Therefore, in this contribution, the effects of processing parameters (i.e. time, temperature, Al content and activator content) on CT evolutions are studied. Thus, this is important in two ways; i) the coating microstructure is greatly dependent on substrate chemical composition which relies on the processing conditions and ii) with particular reference to the thickness of the turbine blade i.e. about 1mm, thus higher coating thickness could damage the desired load bearing properties of the alloy (Zhao 2014, Chandio 2015). Moreover, it is further believed that higher aluminising temperatures at longer durations might change the substrate mechanical properties by precipitates coarsening (Tsipas, Omar et al. 2008, Tong, et al. 2010); however, this aspect is the out Dengzun of scope of present work which will be published separately. Nevertheless, it demonstrates that coating processing is important to both the oxidation resistance and substrate mechanical properties.

METHODS

In this study, second generation single crystal CMSX-4 super alloy was used for the deposition of β Ni Al coatings of whose composition is given in (**Table 1**). The aero engine super alloy blade samples were provided by Rolls Royce Plc, United Kingdom. The

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coating substrates were prepared by sectioning the blade into $10 \ge 10x2$ mm discs (or in some cases 10x15 mm); this was followed by mechanical grinding operations from 240 to 1200 grit emery papers. Finally, alloy samples were washed, degreased, ultrasonically cleaned and drying was carried out in a vacuum before coating formation.

The coating deposition was carried out using in-situ CVD method at various pack mixture compositions. The main pack compositions include; alumina (Al_2O_3) , activator (NH₄Cl) and aluminium (Al). More details of

the aluminising temperature, pack mixture and procedures have been found elsewhere (Goward GW 1979) (Goward 1971) (Xiang 2001). It should be noted that before analysis, all of the coatings deposited at different temperatures (**Fig. 1a**) under gone an annealing at 1150°C for 3 hrs (**Fig. 1b**) in a high vacuum furnace. The FESEM, (Philips XL30) with EDS, powder XRD (Philips X'pert PANalytical) and energy dispersive X-ray fluorescence spectroscopy (EDXRF, MiniPal) were utilised for the study of microstructure and chemical composition, phase and surface chemistry of the coatings, respectively.

Table 1 presents the chemical composition of a second generation single crystal CMSX-4 super alloy (Cannon-Muskegon Corporation, USA).

	Co	Al	Re	Cr	Ti	W	Та	Hf	Ni	Мо
Wt. %	9.60	5.64	2.90	6.40	1.0	6.40	6.60	0.1	61.42	0.6
At. %	9.2	12.6	1.0	7.6	1.3	2.0	2.2	0.03	63.8	0.4



Fig. 2 shows the coating processing temperatures; (a) aluminising temperatures and (b) diffusion annealing cycle.

3. <u>RESULTS AND DISCUSSION</u> 3.1 Microstructure, Composition & Phases of Coating

(Fig. 3a–d) shows the cross-section of the β NiAl coating in as-deposited and its line scan from top to bottom and XRD spectrum. These coating samples were taken randomly in order to confirm the formation of desired coating phase. It consists of two layers i.e. outer and inner (or inter diffusion zone, IDZ). Both layers are rich α -Cr precipitates as shown in (Fig. 3b) (Moskal 2009). It is the characteristic microstructure of the β Ni Al kind BC. The EDX lines can was also performed along the cross-section through the BC thickness which

shows the presence of several elements in β NiAl coating. These include, Cr, Co, W, Ta and Ti other than the standard Ni and Al. The bulk coating analysis was also carried out using EDXRF which further confirms the presence of substrate elements in coatings as shown in (Table 2).

Table 2 presents the surface chemical composition of a typical high activity β NiAl coating produced in this study.

	Al	Cr	Со	Ti	W	Та	Ni
At. %	49.5	3.50	4.90	1.1	4.10	2.15	Bal.



Fig. 3 shows the as-deposited coating: (a) SEM micrograph showing the typical two layered coating, (b) presents the magnified electron micrograph depicting the typical α-Cr precipitates, (c) EDS concentration profile in the form a line scan measured from top to bottom shows several other elements in coating entrapped from substrate and (d) X-ray spectrum indicating the coating phase as βNiAl.

Moreover, from XRD pattern, it further confirms that the coatings formed presently consist of the β NiAl structure in the as-deposited condition. From both SEM and XRD observation, it demonstrates that coatings formed presently are typical of high activity low temperature (HALT) aluminising process (Goward 1979).

3.2 Time Vs Coating Thickness (CT)

The time of deposition is also commonly called aluminising time or process time. This allows the control over coating thickness used in turbine blades. (Fig. 4) shows the coating thickness versus aluminising time. It appears from figure that as the time of coating increased, the CT increased consequently. But, after some time (10hrs),it went off (levelled off). Thus, it implies that the mixture used for coating formation was finished ammonium chloride being an activator. This is believed to one of the demerits of the process utilised presently (Sudhangshu 2011). However, on the contrary to the standard CVD technique, the thickness could be high as desired. Indeed, itis due to the AlCl vapours that are created continuously in an external CVD reactors (Sudhangshu B 2011). In previous works, it is known that the processing time could exhibit profound influence on coating thickness (Sudhangshu B 2007), which confirms to present work.



Fig. 4 shows the CT versus processing time plot for deposition of the β NiAl coatings. It appears quite clear that after 10 hours of aluminising CT does not change significantly.

3.3 Temperature Vs CT

Fig. 5 shows the CT versus processing temperature diagram. From plot it shows that at 800 to 950 °C, the thickness increase is significant. Thereafter, the CT shows variable trend i.e. it increases initially and reduces thereafter and finally attains steady state. This is because, the coating produced at first temperature range, are termed as high activity (HA), while at/beyond 1000°C to 1200 °C, it is called as low activity (LA). This could mean that the temperature of aluminising can change the activity of Al and Ni (or process activity) which are main diffusing species during coating formation process (Goward 1971). The first coating of the HA process is δ -Ni₂Al₃thtcan be spread deep into substrate and thus allowing thick coatings. In contrast, the LA BCs are general beta phase (BNiAl) that grow slower than that of the HA counterparts. Hence, this has been excellently illustrated by Goward and co-workers (Goward 1971). Therefore, it demonstrates that the choice of the BC temperature will be an instrumental to the coating types formed in either process i.e. HA or LA.



Fig. 5 shows the CT versus processing temperature plot. The coating thickness was found to increase from 800 to 1000°C, thereafter reduction is seen due to change in Al and Ni activities.

3.4 Al Content Vs CT

In (Fig. 6) that shows the in-situ CVD Al content versus CT plot at fixed (constant) time and temperature. Initially, from 2 to 6 wt. %, the incremental growth trend was observed. This is because; there is a sufficient amount of Al present in aluminising mixture which facilitates the formation of coating source vapours i.e. AlCl₃ and AlCl, consequently permitting an increased CT. Indeed, the Al content is an instrumental to the deposition of the coating, for example, the PK datta et al. (Xiang 2002, Dong, Yang et al. 2014)reported a minimum 2 wt. % Al in aluminising mixture necessary for coating deposition. This is because; presence of higher Al in in-situ CVD will generate large quantity of halide vapours as mentioned earlier. In contrast, when Al content is reached to critical level, more addition will not alter coating growth significantly. As, this was observed when >6 wt. % Al was used in in-situ CVD

method, hence allowing the steady state growth. Moreover, CT is not the function Al content alone rather the activator and process time together will ensure the formation phenomenon.



It shows clearly that CT is increased sharply from 2 to 6 wt. % thereafter it levelled off, since process attains saturation.

3.5 Activator Content Vs CT

Another important aluminising parameter is the concentration of an activator in in-situ CVD process. Fig. 7 shows the data obtained by adding different concentrations of the activator and resultant CT was monitored at constant time and temperature. A sharp increase in CT was seen from 1 to 3 wt. % of activator. This is due to fact that the activator drives the deposition reactions in in-situ CVD process. In contrast, when > 3wt. % of activator used, no significant change in the CT was observed. On contrary, the more amount of activator caused higher pack pressures witnessed by cracking of the retorts or crucibles. Because, presumably large amount of aluminium halide vapours were generated due to it (activator) and literature suggest having high vapour pressure (Xiang 2004). Therefore, it implies from present observations that a certain level (2 or 3 wt. %) of an activator is capable enough to deposit the desired CT subject to the control over other parameters.



Fig. 7 shows the CT versus activator content plot in in-situ CVD method. It seems that at least> 2 wt. % activator is required to deposit desired quality coatings, in addition to proper control over other processing parameters.

4. <u>CONCLUSIONS</u>

In this study a large number of β Ni Al coatings were successfully formed onto single crystal superalloy using in-situ CVD method. The CT was monitored upon varying the processing parameters. Based on the initial results, following are the concluding remarks; i) at fixed temperature i.e. 880°C, the time of coating deposition was found to have pronounced influence on coating thickness, ii) the temperature range of 800 to 1000 °C was found to affect coating thickness significantly, in contrast beyond that temperature the coating domains (LA and HA)changed causing reduction in CT and iii) coating Al and activator contents were found to affect at initial levels only under the present set of experimental conditions.

ACKNOWLEDGEMENT

The university of Manchester (UoM) and NED University, Pakistan are acknowledged for financial support throughout PhD project. In addition, I would like to thank Rolls Royce UK for providing single crystal superalloy.

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