

Influence of Surface Modification Techniques on Intermetallic Coatings

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Abstract—In this study, nickel aluminide coatings were deposited onto CMSX-4 single crystal superalloy and pure Ni substrates by using in-situ chemical vapour deposition (CVD) technique. The microstructural evolutions and coating thickness (CT) were studied upon the variation of processing conditions i.e. time and temperature. The results demonstrated (under identical conditions) that coating formed on pure Ni contains no substrate entrapments and have lower CT in comparison to one deposited on the CMSX-4 counterpart. In addition, the interdiffusion zone (IDZ) of Ni substrate is a γ' -Ni₃Al in comparison to the CMSX-4 alloy that is β NiAl phase. The higher CT on CMSX-4 superalloy is attributed to presence of γ -Ni/ γ' -Ni₃Al structure which contains ~ 15 at.% Al before deposition (that is already present in superalloy). Two main deposition parameters (time and temperature) of the coatings were also studied in addition to standard comparison of substrate effects. The coating formation time was found to exhibit profound effect on CT, whilst temperature was found to change coating activities. In addition, the CT showed linear trend from 800 to 1000 °C, thereafter reduction was observed. This was attributed to the change in coating activities.

Keywords— β NiAl, in-situ CVD, CT, CMSX-4, Ni, microstructure.

I. INTRODUCTION

SUPERALLOYS used either in land based or aeroengine turbines are designed to provide elevated temperature strength. However, the alloying content used in these alloys do not provide adequate corrosion and oxidation resistance. On contrary, exposure to high temperature or oxidation of superalloys forms complex oxides such as spinels (NiAl₂O₄ etc.). These oxides are non-protective and having high growth rates which are detrimental to their structural integrity. Moreover, the turbine designers use internal cooling system (into turbine blades) to reduce the surface temperature in order to enhance the aeroengine working efficiency. However, to impart both working efficiency and component lifetimes, a coating system is applied. Such coating system is commonly known as thermal barrier coating (TBC) system. It consists of three layers on superalloy; i) ceramic coating as a top coat which is usually known as yttria stabilised zirconia (YSZ), ii) a reaction layer commonly known as thermally grown oxide (TGO) and iii) bond coat (BC) on which TGO is grown. Among these layers, the BC or bond coating or simply metallic coating is of paramount importance. Since, in the absence of a mechanical damage of the TBC, the most failures are attributed to its (BC) performance. Several types of the BC

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materials are proposed and two of them are commonly in practice, i.e. overlay and diffusion type. Furthermore, it should be noted that the superalloys are primarily designed to sustain aggressive high temperature environments while retaining fatigue and tensile strength and essentially creep resistance [1]. But, as mentioned earlier that the alloying content used does not provide high temperature oxidation resistance that needs to be protected while maintaining its load bearing properties. To overcome such problems, heat insulative coatings or TBC systems as shown in Fig. 1 are applied in conjunction to the internal cooling of turbines. Such coating system provides excellent thermal and oxidation resistance. As it was mentioned earlier, TBC is a multi-component system where BC plays an important role. The most common type of the BC used in the TBC is β NiAl based coating. However, the β NiAl BC used for TBC applications usually contains the platinum; nevertheless, its performance is limited by a failure known as rumpling. This is also called roughening of the BC [2]. To a large extent, such rumpling is reduced by the application of fairly new BC, i.e. platinum modified γ/γ' [3]; however, its overall performance is barely comparable to standard platinum modified counterpart [4]. One of the aspects controlling the BC performance is the type of processing used since the nature of coating, aluminum amount, and microstructure are highly influenced by the selection of manufacturing method.

The present contribution is to develop an understanding of the in-situ chemical vapour deposition (CVD) or vapour phase pack aluminising processing conditions which are responsible for BC microstructural evolution and CT changes. In addition, these also depend on type of substrate used for deposition. The objectives of this study are well clear, since it is mandatory to clearly demonstrate the processing conditions of the in-situ CVD process in order to obtain desired quality coatings. This is important for two reasons; i) the microstructure of the coating is highly influenced by substrate composition and ii) the turbine blade whose thickness is about 1mm, therefore the higher CT could impair the useful mechanical properties [5], [6].

II. MATERIALS AND METHODS

In this study, two substrates were used for the deposition of the β NiAl coatings i.e. second generation single crystal CMSX-4 superalloy provided by Rolls Royce Plc, United Kingdom whose chemical composition (in wt. %) is; 9.6Co, 5.64Al, 2.9Re, 6.4Cr, 1.0 Ti, 6.4W, 6.6Ta, 0.1Hf, 61.42Ni and 0.6Mo. Whilst, 99.99% pure Ni rods were supplied by Sigma Aldrich company, USA. The sections or discs of 10 x 10 x 2 mm were prepared by sectioning; this was followed by mechanical grinding operations (240 – 1200 grit). These substrate samples

were washed, degreased, cleaned ultrasonically in ethanol bath and dried in a vacuum oven before deposition.

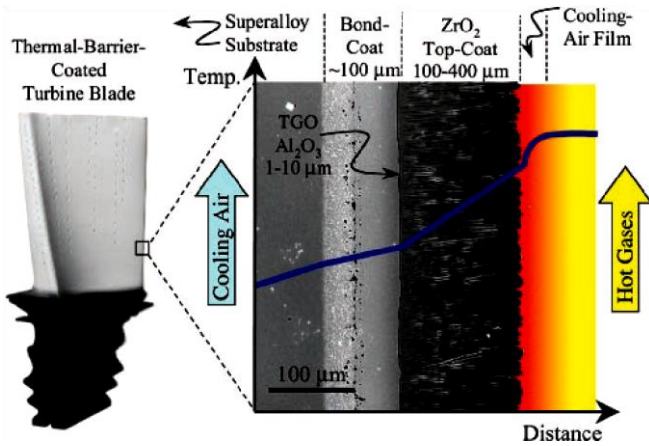


Fig. 1 The cross-section of an EB-PVD TBC placed over a schematic diagram indicating the reduction in surface temperature of turbine

blades by the application of TBC. Thus, outside surfaces of the turbine blades are protected by the TBC system whereas inside/internal one is air cooled provided by internal hollow channels

(in blades) [7]

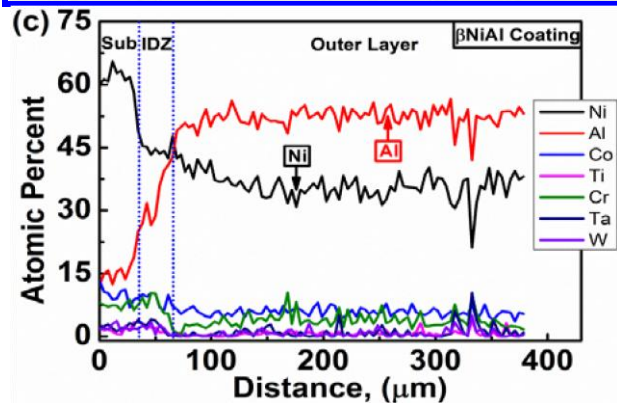
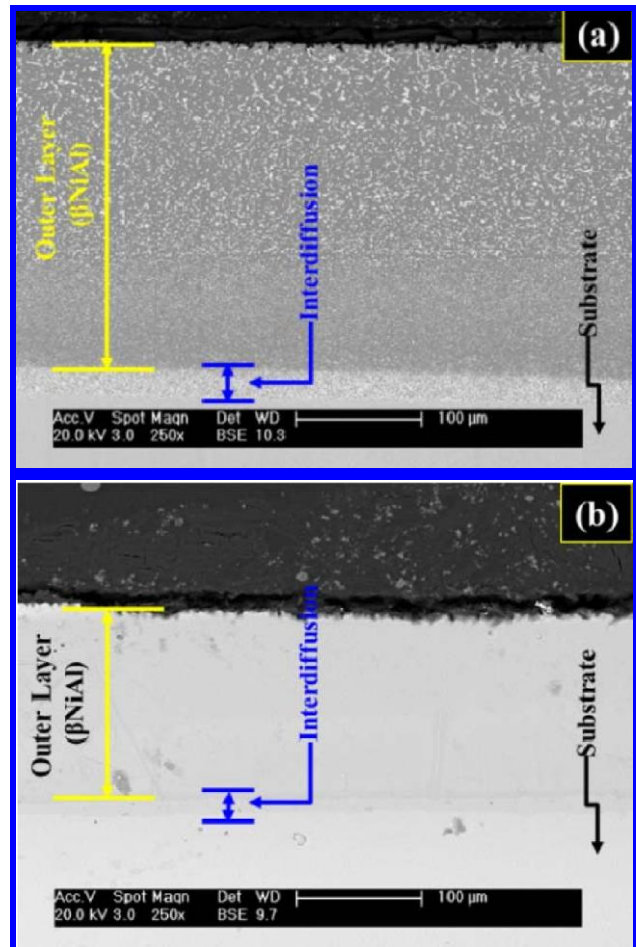
The in-situ CVD method (typically is a high activity low temperature (HALT) aluminising process) was used to prepare coating under identical conditions for both substrates. The coating raw materials include 82 wt.% Al_2O_3 , 3 wt.% NH_4Cl and 10 wt.% Al powder. The details of the aluminising process have been found elsewhere [8]-[10]. In addition, coatings formed on both substrates have received a diffusion annealing treatment at 1150 °C for 3 hours in vacuum furnace ($\sim 10^{-5}$ mbar). For characterisation and analysis, scanning electron microscope (SEM, Philips XL30) coupled with energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD, Philips X'pert PanAnalytical) were utilised in present study.

III. RESULTS AND DISCUSSION

A. As-Deposited Coatings

Figs. 2 (a)-(e) shows the coating cross-sections, concentration profiles and XRD spectra of the coatings in asdeposited condition. In general, both coatings consist of two layered structure, i.e. outer and inner IDZ. It should be noted that the IDZ of coating formed on Ni substrate is a γ' - Ni_3Al phase ($\sim 17.5 \pm 1.5$ at.% Al and 82.5 ± 1.5 at.% Ni) than that of CMSX-4 substrate which is βNiAl phase (37.5 ± 1.5 at. % Al and 62.5 ± 1.5 at. % Ni). The coating formed on CMSX-4 superalloy is rich in typical α -Cr precipitates (bright contrast in Fig. 2 (a) [11]. It is the typical structure of the βNiAl based coatings. On the other hand, coating formed on pure Ni does not contain any entrapment of substrate at large. However, the CT is significantly lower than its alloy counterpart under similar experimental conditions. This is due to fact that CMSX-4 superalloy consists of γ -Ni/ Ni_3Al structure which at an average contains ~ 15 at.% Al. In addition,

presumably the coating formation process is much faster than that of Ni counterpart. This is further confirmed by line scan concentration profiles of both coatings (Figs. 2 (c) and (d)). The coating formed on alloy contains more amount of Al than Ni one. Nevertheless, both coating formed βNiAl as a major as confirmed by XRD observations (Fig. 2 (e)). This is one of the advantages of the βNiAl based coatings which have wide compositional range (refer to Ni-Al diagram for details). Moreover, some minor peaks were not identified so labelled as question mark (?), since they resembled to several phases.



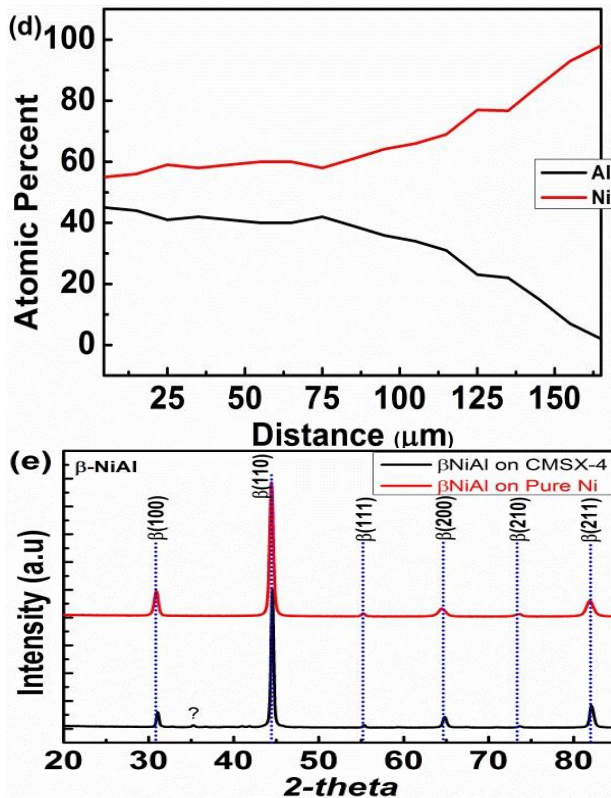


Fig. 2 The as-deposited coating: (a), (b) coating cross-sections formed on CMSX-4 and Ni exhibiting typical two layered structure, (c), (d) EDS concentration profiles of coatings formed on CMSX-4 and Ni substrates that were measured from top to bottom and (e) XRD spectrum indicating β NiAl phase

B. Aluminising Time (AT) versus CT

AT allows the crucial control over CT at fixed temperature. Fig. 3 presents the CT changes upon the variation of AT. It appears clear that as AT is increased, the CT increases accordingly. However, after 10 hours, the CT levelled off. This exhibits that the aluminising mixture has consumed the activator which is known to be one of the demerit of the in-situ CVD technique [12]. In contrast, to CVD method, the CT could be increased as long as it is required. This is because the aluminum monohalide (AlCl) vapours are generated continually in external reactors in CVD system [12]. In literature, it has been also reported that the AT has a profound effect on CT [13] which agrees to this study.

C. Temperature Vs CT

Fig. 4 presents the CT changes plot upon the variation of aluminising temperature. Between 800 to 950 °C, the CT increase is substantial. After that it increased initially and reduced thereafter, and finally more or less levelled off. Indeed, it is due to fact that at the first temperature range, the coatings are termed to be as HALT, whereas from 1000 to 1100 °C, the process is commonly known to be low activity high temperature (LAHT). This implies that the temperature alters the coating formation activities of Al and Ni that are main diffusing species in the process [9]. It should be noted that the initial product of HA process is δ -Ni₃Al which can

penetrate deeper into substrate, hence allowing increased CT upon diffusion treatment. Whereas, the LA coatings are essentially β NiAl based which have comparably slower growth than that of HALT counterparts. In literature, this has been demonstrated by Goward et al. [9]. Thus, it establishes that selection of coating temperature will be crucial parameter to decide the types of the coating produced, i.e. either HALT or LAHT.

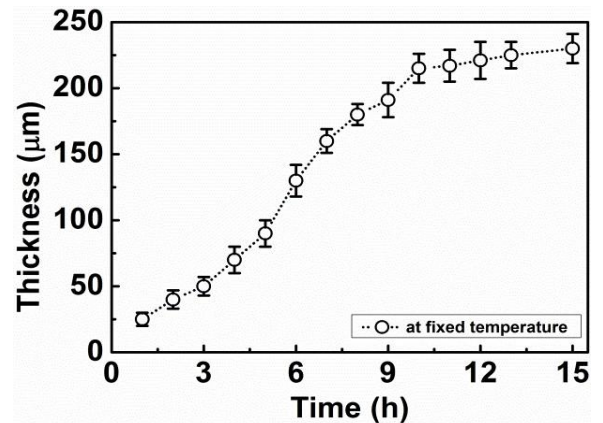


Fig. 3 The CT versus AT plot for deposition of the β NiAl coatings. It appears quite clear that after 10 hours of aluminising CT does not change significantly

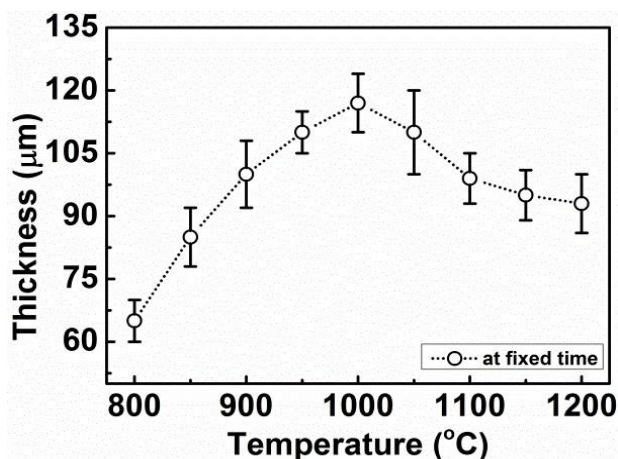


Fig. 4 The CT versus aluminising temperature diagram. It appears clearly that CT increases upon the selection of 800 to 1000°C, this is followed by reduction due to change in process activities

IV. CONCLUSIONS

Based on the experimental results and discussion, the following remarks are concluded at this initial level of investigation. It has been observed that the coating formed on pure Ni contains no substrate entrapments and exhibited lower CT in than that of CMSX-4 single crystal superalloy counterpart. The examination of IDZ on both these substrates shown interesting results. As, the IDZ of Ni substrate coating was found to be γ' -Ni₃Al phase. In contrast, it was β NiAl structure on alloy substrates. Moreover, the higher CT on CMSX-4 superalloy was attributed to the presence of the γ -

Ni/ γ' -Ni₃Al structures, since it contains approximately ~ 15 at.% aluminum. It should be noted that such aluminium amount is before coating deposition that is inherent to superalloy. Some processing parameters were altered, i.e. time and temperature in order to understand their influence on coating quality (in terms of CT). The coating deposition time or AT was found to affect CT significantly, whilst temperature altered the coating activities (HALT and HTLA). In particular, CT showed linear trend in the temperature range of 800 to 1000 °C, thereafter reduction was seen. This was again attributed to change in coating formation activities.

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