Carbides in an aluminised single crystal superalloy: Tracing the source of carbon

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ABSTRACT

Single crystal Ni-base superalloys contain marginal amounts of carbon and as a consequence, diffusion coatings on these superalloys are generally expected to result in carbide free interdiffusion zones (IDZ) containing intermetallic precipitates. The experimentally observed presence of carbides in the IDZ of the aluminised (CVD) single crystal SC2000 led to a thorough investigation of the source of carbon as well as the precipitate phases occurring in the coating and in the IDZ. Scanning electron microscopy (SEM) combined with energy- and wavelength-dispersive X-ray spectroscopy (EDX/WDX) was employed to characterise the aluminised superalloy specimens. Average concentration profiles were determined by glow discharge optical emission spectroscopy (GDOES). Phases were then identified by X-Ray diffraction (XRD) and electron backscatter diffraction (EBSD). The carbides in the interdiffusion zone were found to be of the type $M_6C/M_{12}C$. By aluminising specimens of SC2000 with different thicknesses, the available carbon reservoir for the precipitation of carbides was varied. The amount of carbides in the IDZ after coating decreased with decreasing thickness of the substrate specimen. Hence it could be confirmed that carbon indeed diffused from the substrate to the coating/substrate interface and did not originate from the service environment.

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1. Introduction

High temperature protective coatings on Ni-base superalloys employed in aero engines and industrial gas turbines are essential to extend their operating life in oxidising and corroding environments. Formation of a protective slow growing layer of α-alumina [1] on the coating surface is the key to obtain the required protection. This is achieved by coatings which contain high concentrations of Al provided through Al-rich reservoir phases. The two main types of coatings are classified based on the coating procedure as overlay coatings of the MCrAlY (M = Ni, Co) type [2,3] or diffusion coatings composed of aluminides [4,5]. Overlay coatings are commonly applied by low pressure plasma spraying (LPPS), high velocity oxyfuel (HVOF) or air plasma spraying (APS) [6]. The typical microstructure of the coating mainly consists of the γ-Ni-phase (fcc) and the Al-rich β-NiAl phase (CsCl) [7], however other phases might be present depending on the coating composition and temperature [8,9]. The diffusion aluminide coatings are generally formed by exposing the superalloy to an Al-rich gaseous environment at elevated temperatures to enable diffusion of Al into the substrate or induce diffusion of nickel from the substrate

towards the coating. This results in a coating predominantly consisting of the β-NiAl phase or the non-stochiometric Ni_2Al_3-phase [10]. Aluminide coatings offer an economical alternative in comparison to coatings applied by the plasma spray processes [11].

1.1. Formation of aluminide coatings

The formation mechanisms of diffusion aluminide coatings on Ni-base superalloys were elucidated by Goward and Boone [12]. The authors classified the methods of formation of diffusion coatings by pack cementation as (a) low-temperature, high Al-activity pack and (b) high-temperature, low Al-activity pack. The final coating composition, microstructure and thickness are dependent on the method used. Inward diffusion of Al from the medium into the substrate is the predominant mechanism in the former process as the aluminising medium has a high Al-activity. Hence, the process tends to form Al-rich Ni_2Al_3 which is usually transformed to NiAl during a subsequent diffusion annealing. During the low-activity process, the rate of supply of Al from the medium (with a lower Al-activity) to the substrate is lower than the counter diffusion of Ni from the substrate. Hence, a Ni-rich β-phase (NiAl) is formed. Various studies have been conducted to investigate the influence of pack procedures and parameters on the coating microstructure and performance [13,14,15].

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Table 1
Composition of the as-received single crystal alloy SC2000 in wt.% as determined by ICP-OES and infrared analysis.

Element	Co	Cr	Al	Ta	W	Mo	Re	Hf	C	Ni
Concentration	9.91	4.85	5.63	9.0	6.0	2.0	3.0	0.1	014 ± 0.0058	Bal.

1.2. Phase transformations during aluminising

An obvious conclusion of the diffusion controlled nature of aluminising process is that the substrate composition will influence the coating microstructure. The diffusion of Al from the gaseous environment coupled with the counter diffusion of Ni from the substrate induces diffusion of the alloying elements in the substrate resulting in precipitation of different phases near the coating-substrate interface, generally termed as the interdiffusion zone (IDZ). One of the earlier extensive studies of the influence of alloy composition on the coating microstructure was conducted by Fleetwood [16]. A series of 24 vacuum-melted cast Ni-base alloys with varying concentrations of C, Cr, Mo, W, Nb, Al, Zr and B were aluminised by a pack cementation process. Carbides and/or particles of α-phases containing mainly Cr, W and Mo were observed in the interdiffusion zone of the coated specimens. The lowest amount of carbon in the alloys was less than 0.002 wt.%. No specific information was provided by the authors regarding the influence of the alloy carbon content on phases found in the IDZ of the coated material. Redden [5] selected the three commercial nickel-base superalloys IN 100, SEL 15 and Udimet-700 for aluminising at approximately 1000 °C using a low-activity pack. The phases in the diffusion zone were electrolytically extracted and were identified by X-ray diffraction to be M_6C, $M_{23}C_6$ carbides in low amounts and a significant fraction of MC carbides and σ-phase. In these alloys the minimum carbon concentration in the substrate amounted to 0.08 wt.%. The reason for the precipitation of these phases was claimed to be the observed lower concentration of Ni in the diffusion zone than in the substrate, which results in a decreased solubility of the alloying elements in the interdiffusion zone. Based on the quantity of carbides and the measured element concentrations in the interdiffusion zone, it was furthermore indicated that carbon diffused from the substrate towards the coating/substrate interface during the coating process.

1.3. Phase transformations during high temperature exposure

Al diffuses inward from the coating and Ni diffuses outward from the substrate during the high temperature exposure experiments. The consequence of these compositional changes is a transition of existing precipitates and/or precipitation of new phases. The relative thermodynamic stability of the carbides and intermetallic phases in the IDZ of Ni-base superalloys has been reported by Collins [17]. Collins examined twelve Ni-base superalloys to identify and to determine the relative stability of minor precipitate phases between 760 and 1150 °C up to exposure times of 5000 h. Three types of carbides MC, $M_{23}C_6$ and M_6C, a boride of the type M_3B_2 as well as sigma and μ phases were observed as precipitates in the IDZ, depending on the alloy composition. The minimum initial concentration of C in the alloy was 0.06 wt.%. The μ-phase was observed only in case of René 41 and Unitemp AF2-1D. Sabol et al. [18] concluded that the stability of the carbides ranging from the type $M_{23}C_6$ through M_6C to MC depends strongly on the temperature and duration of exposure.

The concentrations of the refractory metals (Cr, W, Mo, Ta) and the transition metals (Ni, Co) in the alloy also significantly influence the type of stable carbide phases. The addition of refractory elements and strong carbide formers such as Ta, W and Mo generally tends to shift the formation of carbides in the following order [19]: $M_{23}C_6 \rightarrow M_6C \rightarrow MC$. Ettmayer et al. [20] investigated the thermal stability of the η-carbides between 900 °C and 1400 °C in the A–Mo–C and A–W–C

(A = Fe,Ni,Co) systems. The authors came to the conclusion that in the Co–Mo–C system, the $M_{12}C$ carbide Co_6Mo_6C dissociates into $Co_3Mo_3C + \mu$-phase Co_7Mo_6 above 1000 °C. Three types of η-carbides Co_6W_6C, Co_3W_3C and Co_2W_4C were found to co-exist between 1100 and 1350 °C in the Co–W–C system.

The aforementioned investigations dealt primarily with polycrystalline substrates. Single crystal superalloys generally contain a very small or close to a negligible amount of carbon, which is not expected to influence the phases precipitating during the aluminising process. To the best of the knowledge of the present authors, very little has been reported about a possible influence of such low amounts of carbon in single crystal superalloys on the phases formed in the interdiffusion zone during the aluminising process. Gale et al. [21] aluminised the Ni-base single crystal superalloy RR2000 with principal alloying additions of Co, Cr, Al, Ti and Mo and a C content of 0.02 wt.% via a low-activity pack cementation process. $M_{23}C_6$ (M = Cr, Mo) carbides were observed in the coating of composition NiAl. The authors did not however report on the phases formed in the interdiffusion zone.

The current authors observed significant amounts of carbon rich phases in the interdiffusion zone of aluminised single crystal SC2000 specimens. The aim of the current study was to unequivocally characterise the observed phases and trace the source of carbon necessary for precipitation of those phases. This would contribute to the optimisation of the coating process on this type of alloys. Additionally, a better understanding of the post-aluminising degradation of the coating microstructure in-service can be obtained. The experimental procedure used will be described in the following sections. Results of microscopic examination, characterisation and surface analysis of specimens will be shown followed by a discussion.

2. Experimental procedure

Rectangular specimens of different thicknesses (20 × 10 × 2 mm, 20 × 10 × 1 mm and 20 × 10 × 0.5 mm) of the single crystalline Ni-base superalloy SC2000 were aluminised in a high-activity and low-activity pack by an industrially employed chemical vapour deposition method (CVD). The composition of the base alloy was estimated by
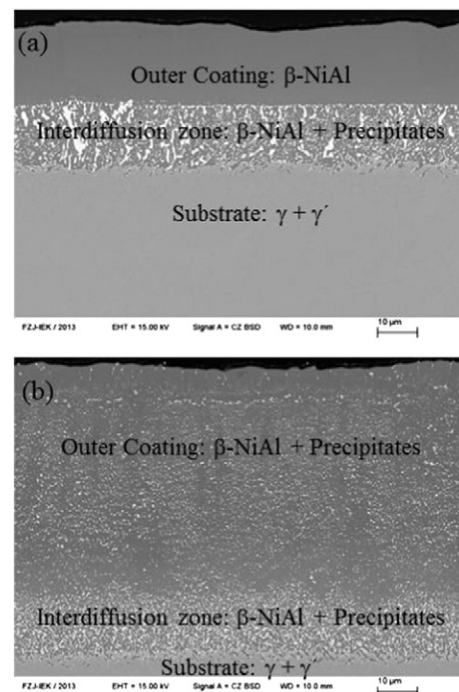

Fig. 1. BSE-images of the cross sections of the as-coated material with the (a) low-activity and (b) high-activity aluminide coatings on the single crystal superalloy SC2000.