



# Characterization of the alumina scale formed on coated and uncoated doped superalloys

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## ABSTRACT

To investigate the mechanisms by which Y and La dopants affect the oxidation behavior of Ni-base single-crystal superalloys, the oxide scales formed on two variants of a commercial X4 alloy, each with and without a MCrAlYHfSi coating were characterized. The alloy systems were oxidized for 100 h at 1100 °C and then examined using analytical transmission electron microscopy. Without a coating, a duplex scale was formed on the superalloy surface comprised of an outer Ni-rich spinel-type layer and an inner columnar  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer. In this case, Hf and Ti were found segregated to the alumina grain boundaries in the outer part of the scale on both alloys but only Hf was detected near the metal–alumina interface. There was no evidence of Ta, Y or La segregation to the alumina scale grain boundaries after this exposure. The scale formed on the alloys with the thermally sprayed coating was primarily alumina, and Y and Hf segregated to the alumina grain boundaries for both alloys. There was evidence of Ti-rich oxides in the outer part of the scale indicating that Ti had diffused through the coating into the thermally grown oxide but La was not found.

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## 1. Introduction

Indigenous sulfur and reactive elements are known to have a strong effect on the formation of alumina scales on single-crystal Ni-base superalloys [1–8]. Typically, S levels are kept below a few ppm and RE additions are <0.05 at.% for optimum behavior. The use of RE “co-doping” has recently been emphasized as a strategy for optimizing the oxidation resistance of superalloys, conventional alloys, and coatings [8–13]. In conventional alloys, the benefit of co-doping can be quantified by observed increases in lifetime (i.e. time to breakaway oxidation). For superalloys, the RE co-doping benefit can be realized in an extended time to significant scale spallation or as an increase in the lifetime of a thermal barrier coating (TBC). However, the TBC bond coating can also contain REs in addition to the superalloy REs. Recently, it was reported that very low levels of Y and La in a second generation, single-crystal, Ni-base superalloy could increase TBC lifetime significantly [8,13].

The mechanism by which RE additions improve scale adhesion has been debated for many decades [14]. There is little doubt that the segregation of these oxygen-active elements to scale grain boundaries and the metal–scale interface is linked to their positive effect [5,10,11,14–16]. However, it is also widely believed that impurity “gettering”, e.g. a Y–S interaction, prevents S from segregating to the metal–scale interface [1–4,17]. This is why Y additions,

along with Hf, are commonly found in second-generation, single-crystal superalloys, combined with low S levels [2–8]. A further addition of La [8] may also be added to getter P, however, there is little experimental evidence regarding the effect of P on scale adhesion or a La–P interaction. In order to begin assessing the mechanism by which Y and La additions affect the oxidation performance of second-generation, single crystal superalloys, the present study examined segregation of REs to alumina grain boundaries in the scales formed on La- and/or Y-doped superalloys with and without a NiCoCrAlYHfSi bond coating [9,16,18].

## 2. Experimental procedure

Three different variations of single crystal, second-generation superalloy CMSX4, were characterized and their compositions are given in Table 1. Bare (no coating) X4 and X4 + La coupons (~16 mm diameter × 1.5–2.0 mm thickness) with a final 0.3 µm polish were characterized after isothermal oxidation for 100 h at 1100 °C in dry O<sub>2</sub>. Specimens of X4\* and X4 + La were spray coated using a high-velocity, oxygen–fuel (HVOF) process with MCrAlYHfSi (PWA 286 composition). The starting powder composition is also given in Table 1.

Coated coupons were annealed for 4 h at 1080 °C in vacuum and the coating thicknesses are given in Table 2. The coating roughness was R<sub>a</sub> ~ 5 µm as-annealed and so specimens were given a light polish with 0.3 µm alumina to assist in specimen preparation for transmission electron microscopy (TEM). Oxidation conditions for the coated specimens were the same as for the bare specimens. All coupons were

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**Table 1**

Chemical composition in wt.% determined by inductively coupled plasma and combustion analysis.

Alloy	Ni	Co	Cr	Al	Fe	Hf	Ti	Y	La	Mo	Re	Ta	W	Si	S	P
X4	60.83	9.47	6.4	5.8	0.05	0.08	0.96	<0.0003	<0.01	0.59	2.90	6.49	6.39	0.02	<0.0001	<0.002
X4*	63.03	10.32	5.54	<b>4.16</b>	0.03	<b>0.18</b>	1.02	0.0004	<0.01	0.61	2.81	6.31	5.97	<0.01	<1	<0.002
X4 + La	61.08	9.55	6.27	5.69	0.03	0.08	0.97	0.0014	0.0009	0.59	2.81	6.54	6.32	0.01	<0.0001	<0.002
PWA286 (powder)	48.02	21.55	16.71	12.26	0.04	0.25	<0.01	0.682	<0.01	<0.01	–	<0.01	0.01	0.36	0.0002	0.013

ultrasonically cleaned in acetone and ethanol before exposure in a Cahn model 1000 microbalance.

After exposure, the surface of the specimens was examined by scanning electron microscopy (Hitachi model S4800) and phases determined by x-ray diffraction (XRD). The specimens were then Cu-plated and metallographically prepared in cross-section for analysis by electron probe microanalysis (EPMA) using a JEOL JXA-8200 with wavelength dispersive x-ray analysis. Thin samples for TEM examination were prepared via the focus ion beam (FIB) in-situ lift-out technique using a Hitachi NB5000 FIB-SEM and were characterized in the TEM by selected area electron diffraction (SAED) and EDS analysis using a Philips CM-200 scanning transmission electron microscope (STEM) equipped with a Schottky field emission gun (FEG) operated at 200 kV and an FEI Tecnai Osiris equipped with an XFEG gun (the latest generation Schottky source) and an A-twin pole-piece integrated Bruker SuperX silicon drift detector (SDD) EDS system.

### 3. Results and discussion

#### 3.1. Microscopic characterization

The mass change data for the four specimens exposed for 100 h at 1000 °C (two bare alloys and two coated superalloys) are given in Table 2. Example plan-view SEM images of the surfaces of the exposed alloys are shown in Fig. 1. Because the scale formed in each case was similar, only examples from one superalloy are shown. Without a coating, the polished surface formed a very flat, adherent oxide in both cases and the Ni-rich outer transient layer morphology can be seen in Fig. 1b. The rougher coated surface showed scale spallation in both cases. The backscattered secondary electron (BSE) image highlights the spalled areas and the higher magnification image shows the fine alumina morphology, likely a mixture of re-grown oxide after spallation (Fig. 1d). Both XRD and electron diffraction analyses indicated that  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was present in all cases.

Optical cross-section images of the bare X4 and X4 + La superalloys are shown in Fig. 2a–b. The scale thicknesses are similar in both cases. The scale thickness formed on bare X4 + La superalloy is slightly thinner when compared to the scale formed on bare X4, which shows

a positive effect of La + Y addition. In both samples (X4 and X4 + La), a denuded zone was observed with a depth of ~3  $\mu$ m beneath a two-layered oxide scale structure as measured through EPMA line scans (Fig. 2c). However, using TEM,  $\gamma'$ -precipitates were still present within this zone as evident in the selected area diffraction (SAD) pattern (Fig. 2d), which showed superlattice  $\gamma'$  reflections in addition to the  $\gamma$  reflections. The  $\gamma'$  reflections are diffuse which might indicate short range ordering.

EPMA elemental maps from the bare X4 + La cross-section are presented in Fig. 3. The maps show the depletion layer and that the inner oxide layer is primarily alumina and the outer layer contains Ni, Al, Cr, Ti and Ta, typical of a spinel-type oxide. In the depletion layer, Ta and Ti also appear to be depleted. The Hf map (Fig. 3d) indicates that the small oxide pegs at the metal–scale interface are due to Hf internal oxidation.

Optical cross-section images of the oxidized coated specimens (X4\* and X4 + La) are shown in Fig. 4. The roughness of the coating resulted in a non-uniform alumina scale that appeared similar in thickness in each case (Table 2). A companion study of the same coatings and substrates reported no change in oxide thickness or adhesion for these two alloys exposed for 500, 1-h cycles at 1100 °C [18]. Table 2 also gives the change in the coating thickness and interdiffusion (ID) zone for each substrate alloy. Because of the relatively short exposure time (100 h), a complete  $\beta$ -denuded layer has not developed. Fig. 4 shows some entrapped oxides in the coating, especially at the original substrate interface. Fig. 4c and d show higher magnification BSE images that emphasize the two-phase coating structure with entrapped the alumina particles (marked on the image with arrows).

#### 3.2. TEM characterization

Fig. 5 summarizes the TEM observations for the four cross-sectioned samples that were oxidized for 100 h at 1100 °C. Table 2 gives the average thicknesses for the inner and outer layers for each case measured from the TEM images. As shown in Fig. 5a and b, the bare superalloys demonstrated the expected dual-layer oxide structure, while the coated substrates (Fig. 5c and d) formed only an alumina layer. In all cases, the alumina layer had a columnar grain structure and was identified by SAED as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

For the bare superalloys, numerous precipitates are present that were not clearly observed by SEM or EPMA. EDS maps of the scale formed on bare X4 + La are shown in Fig. 6. The outer spinel-type layer is primarily comprised of Ni, Cr and Al and SEAD and x-ray diffraction confirmed a Ni(Cr,Al)<sub>2</sub>O<sub>4</sub> spinel-type structure. Oxide precipitates, rich in Ta, Hf and Ti, were observed at the gas interface, consistent with the outward transport of these oxygen-active elements [14] with the highest concentration in the alloy. Near the center of the outer oxide layer, there is a row of oxide precipitates that contain a number of different elements (Hf, Ti, Ta, Cr). Also, there are numerous pores at the alumina–spinel interface, which is similar to prior observations [5,10,11,19,20].

Table 2 indicates that the alumina layer was slightly thinner for the La-doped alloy compared to X4. The Hf map in Fig. 6 shows Hf segregation on many of the columnar grain boundaries. Figs. 7 and 8 present higher magnification maps near the metal–alumina scale interface for both uncoated alloys. In both cases, only Hf was observed to segregate to the grain boundaries. However, both Ti and Hf were observed to

**Table 2**

Mass change data with thickness measurements of the oxide scale, coating and ID zone for bare and coated alloys in as annealed and in annealed and oxidized conditions.

Material	Conditions	Mass change (mg/cm <sup>2</sup> )	Oxide thickness ( $\mu$ m)				Coating ( $\mu$ m)	ID zone ( $\mu$ m)
			Total	Outer layer	Inner layer			
			by SEM	by TEM				
X4	Oxidized <sup>2</sup>	0.51	5.7	4.7	2.7	2.0	–	–
Coated	Annealed <sup>1</sup>	–	–	–	–	–	134	5
X4*	Oxidized	1.16	4.1	3.1	3.1	–	112	48
X4 + La	Oxidized	0.53	3.9	3.6	2.3	1.3	–	–
Coated	Annealed	–	–	–	–	–	130	5
X4 + La	Oxidized	0.99	4.8	3.3	3.3	–	114	56
LPPS on 1484	Annealed	–	–	–	–	–	140	5
	Oxidized	–	–	1.8	1	0.4	–	20

<sup>1</sup>Annealed condition: 4 h/1080 °C.<sup>2</sup>Oxidized condition: 100 h/1100 °C.

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