



Regular Article

The effect of boron on oxide scale formation in a new polycrystalline superalloy



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ABSTRACT

Boron addition to a new polycrystalline nickel-based superalloy promotes the formation of a hitherto unreported aluminoborate phase, in the scale produced by oxidation in air at 900 °C for ~10,000 h. Atom probe tomography provides unambiguous confirmation of this. The ramifications of its formation are discussed.

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Very little is known about the role played by grain boundary elements such as boron on the oxidation behaviour of the nickel-based superalloys [1,2]. The difficulty in detecting this element – particularly at the necessary spatial resolution – has contributed to this situation. Traditionally, electron microscopy and/or X-ray diffraction have been used for the characterisation of the oxidation reaction in these materials [3]. Consequently, the collection of accurate chemical composition data for boron from oxides is not generally deemed feasible. Peak overlapping issues in the case of certain elements – such as chromium and oxygen – also present difficulties. However, recent improvements in analytical techniques – such as atom probe tomography (APT) – allow in principle more accurate measurements. Atom probe tomography is a 3D characterisation method which provides chemical resolution on the nanoscale. It has great potential to generate invaluable insight into the chemistry of oxides [4–6].

Nevertheless, analysis of brittle, thermally and electrically insulating samples using the APT method is still in itself very challenging. In-depth studies therefore of oxidation behaviour which encompasses 3D distributions of chemical compositions and segregation are rather limited and rare. But recent developments both in instrumentation and sample preparation techniques are now facilitating APT measurements on oxide scales [7,8]. In the present study, a multi-scale investigation was performed using a suite of characterisation techniques to provide an understanding of the oxidation behaviour of a boron-containing polycrystalline superalloy.

A recently developed polycrystalline superalloy suitable for power generation applications was used in this study, known as STAL15-CC

[9], see Table 1. After conventional casting, a hot isostatic press (HIP) – at 1195 °C for 5 h under 175 MPa pressure – was used to consolidate the as-cast bars, to eliminate microporosity and improve mechanical properties. The process of HIP was followed by a stage of primary ageing at 1120 °C for 4 h and a subsequent second stage of ageing at 845 °C for 24 h, both followed by air-cooling. Fully heat-treated specimens of 10 mm × 15 mm × 3 mm thickness were isothermally exposed at 900 °C in air for ~10,000 h.

An overview of the morphology of the oxide – obtained using a Zeiss Merlin field emission gun-scanning electron microscope (FEG-SEM) – is illustrated in the backscattered SEM micrograph of Fig. 1. Careful examination of the scale indicates three different oxide layers; a schematic representation of the oxide scale is given. To provide a first insight into the composition of the oxide layers spot analyses were performed within each layer using a Zeiss Merlin microscope, at 4 keV. The red boxes in Fig. 1(a) indicate areas for energy dispersive X-ray (EDX) spot analysis with the corresponding spectrum shown in Fig. 2(a). The internal layer was found to be Al-rich as illustrated in Fig. 2(a) and it has formed a continuous layer. This is consistent with the data of Sato *et al.* [10] who investigated previously the oxidation character of the single crystal version of STAL15 – which for the avoidance of doubt is not doped with boron. There, a continuous alumina Al₂O₃ layer was confirmed by SEM, X-ray diffraction (XRD) and transmission electron microscopy (TEM) in specimens exposed at 900 °C for 100 h. Thus the formation of the alumina layer is expected in the conventional cast version of STAL15, confirming the strong alumina-forming characteristics of this system.

But in the boron-doped STAL15-CC considered here the intermediate oxide is enriched in boron, see Fig. 2(b); its Al content is less than in the alumina below it. Note that the Cr content cannot be evaluated

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Table 1
Chemical composition of the STAL15-CC investigated in this work (at.%).

B	C	Co	Cr	Mo	W	Al	Ta	Hf
0.05	0.47	5.50	16.55	0.59	1.26	10.09	2.40	0.02

due to overlapping between the oxygen and chromium peaks at such low keV EDX levels. The outer oxide was found to be enriched in nickel, whereas the aluminium content is decreased still further. Within the detection limits of the EDX method, there was no indication of boron being incorporated in the outer oxide.

Atom probe tomography circumvents the challenges associated with the EDX method and thus provides quantitative information concerning the compositions of the intermediate and outer oxide. Site specific lift-outs were prepared for atom probe tomography from the boron and nickel-rich oxides, using procedures described in Ref. [11]. Samples were analysed using a Cameca LEAP 5000 XR instrument operating in laser mode with pulse rate at 100 kHz, pulse energy 50 pJ and temperature 50 K.

The compositions measured by APT for the boron and nickel-rich oxides are given in Table 2. The outer oxide corresponds to a spinel phase with a stoichiometry of Ni(Al,Cr)₂O₄. In the case of the intermediate oxide, the stoichiometry corresponds to Al₄B₂O₉ [12]; this aluminoborate phase has not been reported before in oxidised nickel-based superalloys. Recently a different boron oxide with a stoichiometry

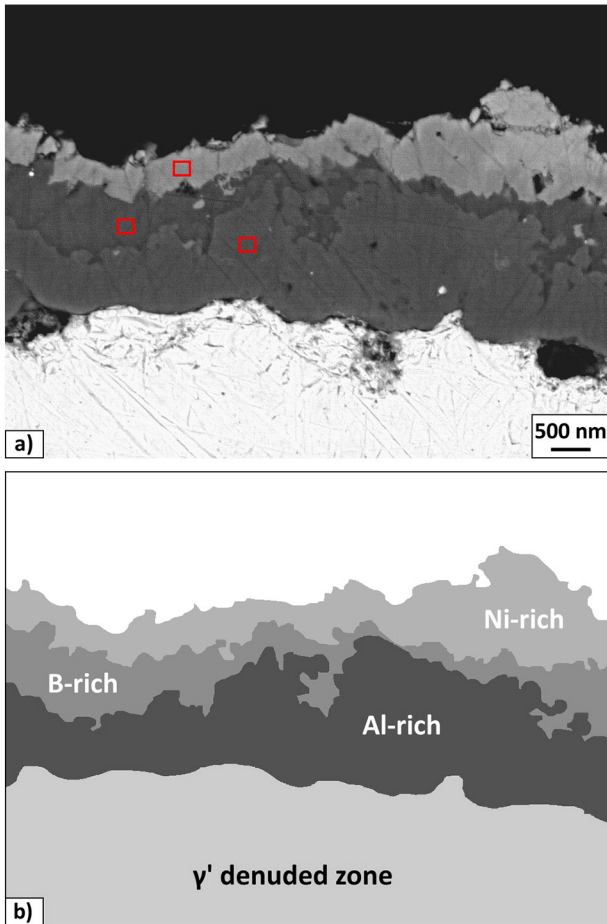


Fig. 1. Specimen from the boron-containing STAL15-CC alloy exposed isothermally at 900 °C for ~10,000 h: a) backscattered SEM micrograph of the oxide scale and b) corresponding schematic representation of the oxide scale. The red boxes denote the areas of point EDX analysis (see data in Fig. 2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

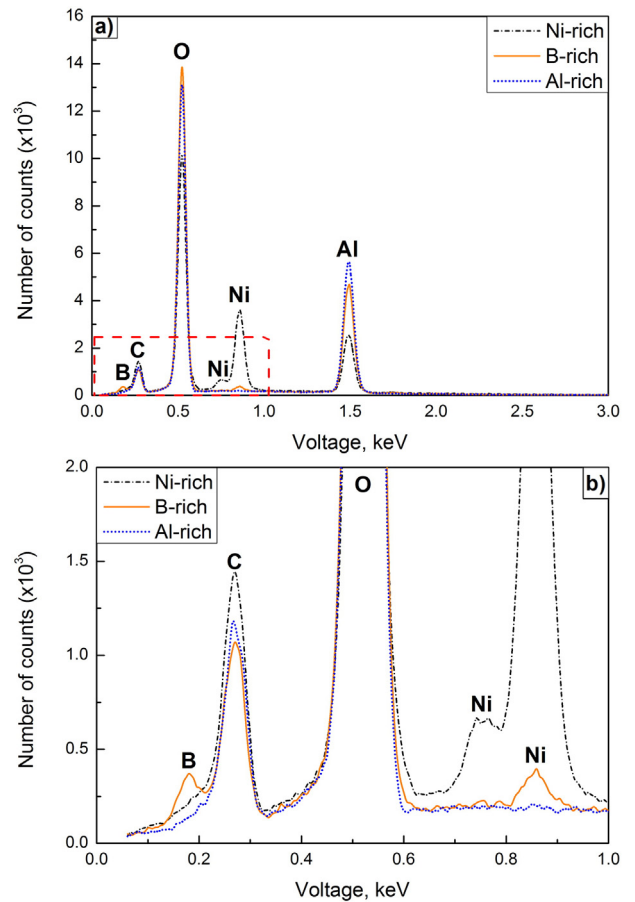


Fig. 2. a) Point EDX analysis corresponding to the oxide areas denoted by the red boxes in Fig. 1 (a) and b) detail of the part of the EDX spectrum as denoted by the red dashed box. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of BCrO₃ was observed in the polycrystalline nickel-based Rene 80 after exposure at 1050 °C resulting in substantial boron depletion after 100 h; such type of oxide was not observed in the current study [13].

The formation of the oxides observed in the current study has been rationalised using thermodynamic calculations, see Fig. 3. The possibility for formation of all major oxide and metallic phases was accounted for in the calculations, which were carried out using the Thermo-Calc software coupled with the TCNI8 and SSUB5 thermodynamic databases [14]. The oxygen activity (content) in the system was controlled by replacing the nickel (for the outer spinel layer) or the nickel and chromium (with atomic ratio of 2:1) for the inner layer where chromium depletion due to outward growth nature of Cr-rich spinel can occur (oxygen activity at the Al₄B₂O₉ & spinel interface is calculated to be approximately 10⁻¹⁰). Note that the amount of Cr₂O₃ predicted (short-dot line in Fig. 3) depends on such depletion which has a time-dependent character. Therefore, the evaluation of Cr₂O₃ formation at the oxide scale needs to be investigated at shorter exposure times. An aluminoborate phase (Al₄B₂O₉) is clearly predicted by the thermodynamic calculations which is stable between the internal Al₂O₃ layer and the outer spinel scale. The formation of the aluminoborate phase would require the

Table 2
Chemical composition of the oxides as measured by APT (at.%).

	Al	B	Cr	Ni	Si	O
Al ₄ B ₂ O ₉	25.0	12.1	2.2	0.1	0.4	60.0
Ni(Al,Cr) ₂ O ₄	5.7	–	27.2	10.1	0.1	56.9

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