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Analysis of surface scale on the Ni-based superalloy CMSX-10N and proposed mechanism of formation

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Abstract. There is a continuing demand to raise the operating temperature of jet engine turbine blades to meet the need for higher turbine entry temperatures (TET) in order to increase thermal efficiency and thrust. Modern, high-pressure turbine blades are made from Ni-based superalloys in single-crystal form via the investment casting process. One important post-cast surface defect, known as 'surface scale', has been investigated on the alloy CMSX-10N. This is an area of distinct discolouration of the aerofoil seen after casting. Auger electron and X-ray photoelectron spectroscopy analysis were carried out on both scaled and un-scaled areas. In the scaled region, a thin layer (~800nm) of Ni oxide is evident. In the un-scaled regions there is a thicker Al₂O₃ layer. It is shown that, as the blade cools during casting, differential thermal contraction of mould and alloy causes the solid blade to 'detach' from the mould in these scaled areas. The formation of Ni Oxides is facilitated by this separation.

1. Introduction

Superalloys are a class of material that have been specifically developed for high temperature applications for use in aero-engines and land-based power generation. The enhanced high temperature strength is principally derived from ordered γ' precipitates with optimum size and morphology. Superalloy chemistry has evolved over the last forty years, primarily with the increasing addition of refractory elements such as Ta, W and Re [1]. The main benefit of these refractory elements is to improve solid solution hardening and to enhance microstructural stability at elevated temperatures. Simultaneous innovations in material processing have resulted in a progressive migration from equiaxed to directional and single-crystal (SX) solidification, where the primary orientation of the grain is aligned along the turbine blade or stress axis [2]. Turbine components are cast in SX form via investment casting and following cast, a thin layer with "fish-scale" appearance and texture is always present across a portion of the turbine blade (TB) aerofoil. Owing to this texture, it is commonly referred to as "surface scale". The extent of surface coverage is dependent on the geometry and length of the aerofoil; extent of surface scale on low-pressure and intermediate-pressure TB's is much greater than on the shorter, high-pressure TB's. Figure 1 is a schematic of a TB directionally solidified with the Ni-based superalloy CMSX-10N. The surface scale is clearly "tongue-shaped" having a pale green discolouration and is most notably present on the convex surface of the aerofoil. The remainder of the aerofoil is referred to as "un-scaled".

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The causes of surface scale in Ni-base superalloys are not well documented, although the role of carbon in suppressing surface scale has been investigated, identifying a threshold of 450ppm carbon in directionally solidified castings beyond which surface scale is suppressed [3]. This suggests that the formation of surface scale could be attributed to a mould-metal reaction. Mould-metal reactions are important considerations in the casting of reactive metals or alloys. Frye et al. [4] have classified possible mould-metal reactions that involve an oxide at the mould interface (M_xO_y) reacting with an element in the liquid alloy (N) to form an oxide (N_xO_y) and dissolution of the displaced element, M. However, these reactions are only prevalent if the resultant oxides are characterised with large negative free energies of formation. Reports of mould-metal reactions in Ni-base superalloys are sparse; the most notable being the study of Piwonka [5], which reports the reaction between the Ni-base superalloy Rene 80 and a zirconia and silica base ceramic. It is argued that Al, Ti and Hf from the liquid alloy can react with the silica (SiO_2) to form alumina (Al_2O_3), which can account for an Al denuded zone in the vicinity of the casting surface.

Figure 1. Schematic representation of a directionally solidified turbine blade showing spatial location of scale (dark region) with photographic insert.

The occurrence of surface scale has a significant impact on the post-processing of as-cast turbine components. In the case of TB's, which operate at the most demanding high temperatures and stresses, the blades are heat-treated in order to homogenise the as-cast microstructure and obtain the optimum γ' morphology. In the case of static components, such as nozzle guide vanes (NGV's), where high temperature properties are less stringent, the components are used in the as-cast form. In both cases there are specific processing issues:

- During heat treatment of TB's, incipient melting of the underlying microstructure just beneath the layer of surface scale is observed. This melted and re-frozen layer has to be subsequently removed using a grit blast operation before the component can be etched to assess the grain structure.
- In the case of NGV's, visual inspection of the components metallurgical integrity is required. Areas exhibiting scale must first be grit blasted to obtain a uniform surface finish and facilitate inspection.

It follows therefore that two scenarios may arise:

1. For a less aggressive blast, the scale remains adhered to the parent substrate and consequently the remnant scale is not attacked by the etch reagent. This etch unaffected region is consequently "opaque" and cannot be inspected for grain defects.
2. For an aggressive blast, there is an accompanying removal of metal from the remainder of the un-scaled surface and this can lead to distortion of the aerofoil geometry in those regions.

The intent of this article will therefore address the following (1) characterisation of both scaled and un-scaled surfaces and (2) the mechanism(s) for the formation of surface scale.

2. Experimental Methods

Single crystal turbine blades were cast from the Ni-based superalloy CMSX-10N using an industrial directional solidification furnace at the Precision Casting Facility, Rolls-Royce plc, Derby, UK. A full description of this process can be found elsewhere [6]. The nominal composition of the alloy CMSX-10N can be seen in table 1. The casting parameters included a furnace temperature of 1525 °C with a withdrawal rate of $6.35 \times 10^{-5} \text{ ms}^{-1}$.

Table 1. Nominal Composition of Alloying Elements (wt.%) in the Ni-Base Superalloy CMSX-10N.

Alloy	Al	Co	Cr	Ti	Mo	Ta	W	Re	C	Ni
CMSX-10N	5.9	3.1	1.6	0.1	0.45	8.5	5.5	6.8	-	Bal

A FEI Sirion 200 Field Emission Gun scanning electron microscope (FEGSEM) was used for secondary electron imaging (SEI) was performed with a working distance of 10 mm and accelerating voltage of 20 kV.

Auger electron spectroscopy (AES) was used to obtain depth profiles from scaled and un-scaled regions of the turbine blade. A JEOL JAMP 7100 microscope was used operating at $\sim 2 \times 10^{-9}$ Torr with a primary electron beam energy of 10 keV focused to a spot $\sim 10 \mu\text{m}$ in diameter with a current of $\sim 0.5 \times 10^{-7}$ A. Sputtering was performed with Ar^+ ions with an energy of 3 keV and current density of $50 \mu\text{Acm}^{-2}$. This results in a theoretical etch rate of $\sim 10 \text{ nm min}^{-1}$. Quantitative analysis was achieved using experimentally derived relative sensitivity factors based on NiO and Al_2O_3 reference samples with an estimated error of $\pm 15\%$.

X-ray photoelectron spectroscopy (XPS) data was obtained using the Scienta ESCA300 instrument at the NCESS, Daresbury Laboratory using monochromated Al $K\alpha$ (1486.7 eV) radiation, a slit width of 0.8 mm and a take-off angle of 90° . Samples were subjected to Ar ion etching by filling the sample preparation chamber with Ar gas to a pressure of $\sim 2 \times 10^{-6}$ Torr. The sample was then exposed to the Ar ion beam for a typical time period of several minutes using an accelerating voltage of 5 kV and beam current of $\sim 200 \text{ mA}$.

3. Results and Discussion

3.1. Surface Characterisation

In order to characterise the microstructure of the surface associated with the scaled and un-scaled regions, SEI's were taken corresponding to these surfaces. For brevity only the boundary region is shown, with the scaled region (left) and the un-scaled region (right). It is observed that there is a marked presence of particles on the un-scaled surface of the aerofoil, seen as white "patches", whilst these particles are absent from the scaled surface. The transition from scaled to un-scaled regions is abrupt in nature with respect to these particles. The elemental composition of a typical particle found in the un-scaled region was determined, using energy dispersive spectroscopy (EDS), to be refractory (ceramic) in nature and enriched in Si, Zr and O [6]. There is also a thin, continuous layer of Al_2O_3 sandwiched between the

Figure 2. SEM image (Secondary electron) of the interfacial boundary showing both scaled (left) and un-scaled surfaces (right).

particles and the substrate. Considering the extensive occurrence of the ceramic particles, a more appropriate characterisation technique, that analyses a greater area, is XPS.

Figure 3. High-resolution XPS data from scaled and un-scaled regions. Spectral regions are; a) Ni(2p), b) Al(2p), c) Re(4f), W(4f) and Ta(4f) (in the same region) and d) Zr(3d).

XPS data was acquired in Ni(2p), Al(2p), Zr(3d), Re(4f), W(4f) and Ta(4f) spectral regions for two samples cut from both scaled and un-scaled areas. The Ni, Al and Zr data is presented in figure 3a, 3b and 3d respectively, while the refractory elements are collectively presented in figure 3c. The un-scaled region shows a very weak signal for Ni(2p) despite the fact that this element represents the bulk component of the alloy. Similarly the rare earth components also show very weak and poorly defined spectral features. In addition a strong signal is observed in the Zr(3d) region. Following these measurements the sample was transferred to the preparation chamber of the XPS instrument and subjected to argon ion milling for a period of 90 minutes. The sample was then returned to the analysis chamber for repeat measurements. A marked increase in the intensity of both Ni and rare earth features is observed with an associated decrease in the intensity of the Zr(3d) component. Quantification of these spectral regions shows Ni:Al:Zr ratios of 1:84:149 in the un-scaled region before Ar ion milling compared to equivalent ratios of 1:24:83 afterwards. In contrast, XPS data from the surface of the scaled sample shows intense and well defined line shapes for nickel and rare earth regions whilst there is no evidence of zirconium. Consequently, the presence of discrete particles enriched in Si, Zr and O on the surface of the un-scaled portion of the aerofoil can be definitively confirmed.

3.2. Chemistry of Scaled and Un-Scaled Casting Surfaces

Given that the thickness of the surface scale is sub-microns, AES was employed for a depth-wise composition characterisation. AES depth profiles were carried out at representative locations within the scaled and un-scaled regions and typical plots are presented in figures 4a – b. In the case of the un-scaled region of the aerofoil, owing to ceramic particles being strewn across the surface, the depth scans were chosen between ceramic particles so that they were not included in the analyses. The following observations can be made:

Figure 4. Auger electron spectroscopy (AES) depth profiling of scaled (a) and un-scaled (b) regions.

It has been shown by Brewster et al [6] that during the initial stages of casting there forms a 0.5-1.5 μm Al_2O_3 layer around the external surface of the liquid metal. This is due to a reaction between the liquid metal and the solid mould prime-coat. However, owing to differential thermal contraction, areas of the metal separate from the mould after it has solidified. The key aspect is that mould-metal separation occurs in the solid-state, unlike the mould-metal reaction, where the metal is liquid. It was found that the alumina layer is retained on the blade surface in the un-scaled regions but, conversely, is retained on the mould wall in the scaled regions. It was also seen that there is an increasing gap width at the convex surface of the aerofoil and also with increasing solidification height.

3.4. Surface scale formation

The detachment of the alumina from the aerofoil surface renders the “bare” metal surface susceptible to subsequent oxidation, resulting in the formation of surface scale. It is important to note that whilst oxidation studies have been conducted on the Ni-based superalloys SRR99 [7, 8] and CMSX-10K (variant of CMSX-10N) [8, 9] these were carried out under atmospheric conditions and for prolonged isothermal holds. For the studies in this paper, the oxygen partial pressures (p_{O_2}) in the casting furnace

Scaled Region: The strongest metallic peaks proceeding inwards from the surface were Ni, Co and Al in that order. There is a strong O that is detected indicating that the scale was oxide and the typical thickness beyond which Ni from the substrate begins to dominate is $\sim 800\text{nm}$.

Un-Scaled Region: The most prominent peaks were Al and O, which indicate the presence of Al_2O_3 , which was also observed by XPS in figure 3b. The thickness of the Al_2O_3 layer is thicker than the oxide in the scaled region.

It should be noted that the C peak relates to contamination from the casting furnace, where the heating elements are graphite.

3.3. Mould/Metal Separation

It can be seen that there are two distinct oxides formed in the scaled and un-scaled areas of the turbine blade, clearly therefore, a simple mould/metal reaction *per se* cannot suitably account for the formation of surface scale that has a distinct predilection for specific areas across the turbine blade aerofoil. It has

(typically 10^{-6} atm) and the hold times are significantly lower. This in turn will affect the species that will be selectively oxidised. In the temperature range; $[700 - 1300]^{\circ}\text{C}$ from the standard free energy of formation of the oxides, the equilibrium p_{O_2} can be determined [10]. The minimum p_{O_2} for oxidation corresponds to NiO, which has the least negative standard free energy of formation and the equilibrium p_{O_2} is given by $[10^{-18} \text{ to } 10^{-7}]$ atm. It follows, therefore, that for the level of vacuum during which directional solidification occurs ($\approx 10^{-6}$ atm), all of the oxide species are stable. Therefore, the type of oxide that forms during such transient oxidation conditions would be mainly dictated by the growth kinetics.

The surface oxide is Ni-rich and therefore most likely NiO. In oxidation studies of CMSX-10N variant alloys [8, 9] similar observations were made. An external layer of predominantly (Ni, Co) O occurs, beneath which various internal spinel phases and then internally oxidised chromium oxide and alumina formed. These observations are similar to the experimental results in this study. The formation of (Ni, Co) O in the scaled region indicates that growth kinetics of NiO dominates, which is consistent with the porous nature of this oxide. Once the external oxide layer has formed, this further reduces the p_{O_2} at the bottom of the scale, thus limiting the species that can form to those with the greatest thermodynamic driving force for formation. This consequently favours formation of chromium oxide and alumina and furthermore the presence of the chromium concentration closer to the surface than the aluminium concentration, is consistent with the oxygen partial pressures required for formation of chromium oxide and alumina. It follows, therefore, that the occurrence of scale on the aerofoil surface refers to the oxide product, which is dependent on the alloy chemistry. It should be clearly distinguished from the mould-metal reaction product that is Al_2O_3 , which is a precursor to oxidation.

3.5. Mechanism for surface scale formation

- (i) After pouring the liquid metal is in contact with the mould prime-coat over the entire blade surface.
- (ii) Mould/metal reaction results in the formation of an Al_2O_3 layer at the casting surface [6].
- (iii) Upon cooling below the solidus temperature, separation of the solidified metal from the mould wall occurs in certain portions of the casting. In these regions the Al_2O_3 layer is stripped away from the metal surface and remains adhered to the mould.
- (iv) As the component cools further, there is oxidation of the “bare” casting surface, which had pulled away from the mould-wall to form an oxide scale.
- (v) When the mould is separated from the casting, small patches of remnant mould prime-coat as well as the Al_2O_3 layer are seen on the un-scaled region.

4. Concluding Remarks

The formation of surface scale during directional solidification has been investigated on the 3rd generation superalloy CMSX-10N and the following conclusions were made:

- The formation of surface scale comprises three steps:
 - (1) formation of a $0.5\text{--}1.5\mu\text{m}$ Al_2O_3 layer around the external surface of liquid metal due to a mould-metal reaction between the liquid and the mould prime-coat,
 - (2) in the scaled areas, separation of the solidified metal from the mould wall during cooling, where the Al_2O_3 layer is stripped away from the metal surface and adhered to the mould,
 - (3) further oxidation of the “bare” metal to form oxide (scale) at surface.
- The scale constitutes the oxides that form on the surface regions that have detached from the mould wall. The scale on CMSX-10N components is predominately nickel rich oxide (likely to be NiO).
- In the un-scaled regions, where the metal has not detached from the mould, the Al_2O_3 layer formed via the mould-metal reaction remains adhered to the solid metal.

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