Formation and Prevention of a Surface Defect on the Aerofoil of As-Cast Nickel-Based Single-Crystal Turbine Blades

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Surface scale is a common casting defect covering up to one-third of the aerofoil on as-cast single-crystal turbine blades. To better understand and control this scale, the scaled and unscaled regions on the surface of a blade are observed. The surface of the unscaled region is covered with a relatively thick and uniform aluminum oxide layer. In comparison, the surface of the scaled region shows a different morphology, which is mainly composed of two different regions: one is a tessellated region with irregular polygons and the other with many irregular lines.

The cross-section and transmission electron microscopy samples of the scaled region clearly show that the surface is covered with double oxide layers of thickness 300–500 nm composed of several metallic oxides, which form after the normal microstructure of the base material during solidification. A specific region, which is in contact with the investment mold but remains in the scaled part, shows the possibility of this scale formation through the reaction of the initial aluminum oxide/mold wall material and the oxidation of the fresh surface of the base material. Based on these observations, the formation mechanism and the prevention of the surface scale are discussed.

1. Introduction

In gas turbines for jet propulsion and electricity generation, higher operating conditions improve fuel efficiency and reduce carbon dioxide emission. To enable this, developing superalloys to withstand the severe operating conditions is required and nickel-based superalloys are the chosen materials due to their mix of properties. Nickel has a face-centered cubic (FCC) crystal structure, which makes it tough and ductile, and importantly the FCC structure of nickel is stable from room temperature to its melting point, which means that there is no phase transformation that would lower the operating temperature, and it also ensures a low diffusion rate, which means low rates of thermally activated creep. To ensure that these alloys can meet the most demanding applications at high temperature, nickel has been alloyed with up to ten other elements.

Nickel-based single-crystal superalloy turbine blades have high mechanical strength and surface stability even approaching their melting temperature and under severe mechanical load. The superior properties of nickel superalloys are attributed to three different size scale strengthening mechanisms: the first one is the atomic-scale solid solution hardening through the addition of soluble elements, which can inhibit dislocation movement; the second one is the nearly micrometer-scale precipitation hardening by the formation of an ordered γ' phase (Ni$_3$(Al, Ta, Ti)) in the γ matrix; and the final one is the millimeter-scale removal of grain boundary by directional solidification, i.e., the formation of a single crystal, which increases mechanical properties by eliminating potential sites of crack initiation and removing a potential creep mechanism of grain boundary sliding and reduces microsegregation and eutectic content.

An investment casting process has been widely used to manufacture nickel-based superalloy turbine blades with superior properties by producing hollow aerofoils with complicated shapes and internal cooling passages. As a result, cooling air can flow inside the turbine blade during operation and consequently, it lowers the superalloy temperature to reasonable levels. In addition, the process produces turbine blades without grain boundaries. The process is comprised of assembling wax models, dipping the model into ceramic slurries, baking the mold, pouring the molten superalloy into the mold, solidifying the metal, and removing the investment shell. The detailed investing process is well described in the literature. Even though this casting process has been used to produce nickel-based single-crystal superalloy turbine blades for decades, several different types of defects still occur in as-cast blades, such as high-angle grain boundaries formed from stray or equiaxed grains driven by poor thermal management or constitutional effects, low-angle grain boundaries through convergence faulting or dendritic bonding, freckle chain grains by double diffusive convection of interdendritic channels with enriched solutes, and surface scale. Much research has been
carried out on some of these defects and consequently, they are relatively well understood. However, there are relatively few studies on surface scale, even though it is the most common manufacturing defect and widely found on the surface of as-cast turbine blades as shown in Figure 1. The surface-scaled region on the aerofoil is easily identified as it often has different colors, such as silver, gold, and black. Even though the affected area slightly differs depending on the blade design, the scale covers almost one-third of the aerofoil region. The scale also exists on both the pressure and suction surfaces of the aerofoil of as-cast turbine blades.

In the investment casting process, a mold is composed of several layers of ceramic slurry (comprising a silica sol with a zirconium silicate flour) and an alumina grit, which makes up the majority of the shell mold. The slurry forms the contact layer for the superalloy melt. However, a strong interaction between the slurry and the melt forms an aluminum oxide layer but it detaches from the base material to reveal a fresh surface during cooling. Finally, subsequent oxidation of the base material induces the surface scale. These strong interaction and formation mechanisms are well understood in the literature.\[9,16\] However, despite this understanding, the surface scale is still a common problem in industry. The surface defect is just removed by abrasive blasting and etching after full heat treatment. However, this mechanical blasting and chemical etching increase cost, and much time and effort are required to completely remove the scale, with the consequential risk of altering the shape of the component. Importantly the current understanding of the surface scale makes it difficult to explain the iridescence phenomenon in the scaled region of a turbine blade, the increased difficulty in the removal of the colored scale above that needed for the gray oxide, and the reasons for the occurrence of two different regions, the scaled and the unscaled, in the same turbine blade and the occurrence of the formation of a scaled region only in the aerofoil part. Furthermore, even though there are several studies on the surface scale, there are few studies on the high-resolution or high-magnification observation of the surface scale itself. Therefore, in this study, the surface of the scaled and unscaled regions as well as the boundary region between them is observed by electron microscopy. Importantly, the cross-section in each region is observed and analyzed to allow a better understanding of the surface defect, the formation mechanism, and finally the prevention of the surface scale.

2. Experimental Section

2.1. Materials

Single-crystal turbine blades were cast in a third-generation nickel-based superalloy (CMSX-10) using investment casting at a production aerospace manufacturing facility. The chemical composition of the alloy is summarized in Table 1. The solidification was conducted at nominally 1773 K (1500 °C) and the vacuum level of the furnace chamber of \( \approx 10^{-6} \) atm. The withdrawal rate was \( \approx 5 \times 10^{-3} \) ms\(^{-1}\), which means that the cast components were exposed at the casting temperature for \( \approx 1–2 \) h depending on the location with respect to the solidification front. These turbine blades containing the surface scale, which can be recognized by dark contrast on the surface (see Figure 1), were removed from the runner system. It is usual that after solution heat treatment, to remove the surface scale, the blades are subjected to several blasting processes, such as dry hone blasting, abrasive blasting and emery dress, and chemical etching. However, in this study, the as-cast turbine blades containing the scale were investigated without any postprocessing.

2.2. Microstructural Characterization

The regions of interest in the turbine blades were cut out by wire-guided electrodischarge machining (EDM) and then ultrasonically cleaned in ethanol for 5 min. Then, these regions were observed using a high-resolution scanning electron microscope (field emission (FE)–SEM, FEI Quanta 3D dual beam FIB–SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX).
system. It was also used for cross-sectioning regions of interest using a focused ion beam (FIB). The images were acquired at two acceleration voltages (5 and 15 kV) but SEM–EDX analysis was performed just at 15 kV.

After SEM observation, transmission electron microscopy (TEM) samples were made by an in situ FIB lift-out technique,\textsuperscript{[17,18]} and observed on a transmission electron microscope (FE–TEM, FEI Tecnai F20) equipped with a scanning mode (STEM) and an EDX system at an operation voltage of 200 kV. An STEM mode was used for STEM–HAADF (high-angle angular dark field) images and STEM–EDX element mapping of interested regions. The base material (CMSX-10) contained ten alloying elements and they suffer from having a close proximity of their characteristic X-rays (M\textsubscript{\alpha}, keV), such as Hf (1.644), Ta (1.709), W (1.774), and Re (1.842),\textsuperscript{[19]} which results in difficulty in clearly distinguishing each element in key areas. Therefore, the chemical composition of these regions was acquired by STEM–EDX with a nominal probe size of about 2 nm averaged from more than ten analysis areas for sufficient statistical confidence, and quantified by the analysis software (Oxford AZtecTEM) installed on the TEM. During TEM observation, the samples were cooled with liquid nitrogen to avoid or minimize microstructural changes in the irradiated area.\textsuperscript{[18]}

3. Results

3.1. General Morphology of the Unscaled and Scaled Region in a Turbine Blade

Figure 1 shows the typical location of the scale formed on the surface of as-cast turbine blades; it can be seen widely on the aerofoil of a turbine blade. A low-magnification SEM image (Figure 2a) shows that the interface of the scaled region with relatively bright contrast and the unscaled region with dark contrast is easily recognized. For comparison a typical unscaled region was selected and cross-sectioned by FIB. The inset in Figure 2b shows a plain view of the selected region, which was far from the boundary with the scale. The surface of the unscaled region is rough and it is known that the surface is composed of a number of ceramic particles, such as zirconium.

Table 1. Compositions of raw material, $\gamma$ and $\gamma'$ phases.\textsuperscript{[26]}

|   | Al | Ti | Cr | Co | Ni | Nb\textsuperscript{b} | Mo | Hf\textsuperscript{a} | Ta | W | Re |
|---|----|----|----|----|----|----------------|----|----------------|----|----|----|
| Raw | 13.6 | 0.1 | 1.8 | 3.2 | 73.7 | 0.0 | 0.3 | 3.0 | 1.9 | 2.4 |
| $\gamma$ | 6.3 | 0.0 | 4.1 | 5.9 | 70.5 | 0.0 | 0.3 | 0.0 | 3.6 | 3.4 | 5.9 |
| $\gamma'$ | 15.6 | 0.1 | 1.0 | 2.7 | 73.6 | 0.0 | 0.0 | 4.6 | 2.4 | 0.0 |

\textsuperscript{a}The exact amounts of Nb and \textsuperscript{b}Hf are 0.04 and 0.001 at\%, respectively.

Figure 2. a) A low-magnification SEM image near the interface of scaled/unscaled regions, b) SEM tilting view images of an unscaled region after cross-sectioning with an insert of a selected region for cross-sectioning far from the boundary of scaled/unscaled after deposition of a platinum layer marked with an arrow, c) SEM tilting-view image at the marked region in panel (b), and d) STEM–EDX point analysis on the marked point in (c) between the protective Pt layer and the base material inside of the scaled region. The arrows in (c) indicate the continuous layer.
silicate and silica originally from the mold material. A protective platinum layer, identified with an arrow in the insert, was deposited on the surface of the selected location and cross-sectioned by FIB. A low-magnification SEM tilting-view image in Figure 2b clearly shows that there is a dark contrast layer between the Pt layer and the base material. It should be emphasized that the magnified image (Figure 2c) of the marked region in Figure 2b confirms that the dark contrast layer is continuous and well bonded to the base material despite the observed surface roughness of the base material. SEM–EDX point analysis (Figure 2d) of the layer indicates that the layer is an aluminum oxide, which is initially formed through the interaction between the melt and the mold material during casting. Above the initial alumina layer, there are ceramic particles with brighter contrasts (see also Figure 9 and 11). This observed continuous aluminum oxide layer protects the base material from further oxidation and consequently, the region remains in an unscaled state, which will be discussed later.

Subsequently, the surface of the scaled region was observed. The scaled region looks smooth during visual inspection of manufacturing components and to an extent this can be seen in the low-magnification SEM observation in Figure 3a, and this is as reported in the literature. However, a tilting view of the scaled region (Figure 3b) clearly shows that it is not microscopically smooth. Also, depending on the analysis position, different spectra of SEM–EDX were acquired (see Figure 4), which implies that the surface of the scaled region is not a uniform surface layer but a mixture or composed of multilayers. It is necessary to observe the scaled region at high magnification and high resolution to better understand the nature of the morphology of this region.

Figure 4 shows the typical morphology of the scaled region acquired at higher magnifications. After thorough scanning of the whole scaled region by SEM, a representative region was selected and investigated (Figure 4a). A magnified image (Figure 4b) of the marked region in Figure 4a shows that the surface looks like a tessellation of irregular polygons bordered by a thin line. SEM–EDX was used to chemically analyze the surface and two representative spectra, respectively, were acquired on the central region (Figure 4c) and the thin line (Figure 4d).

Regardless of the analysis point, strong nickel and oxygen peaks were detected. In addition, considering the intrinsic interaction volume of SEM–EDX with the sample and the probe size, even though the analysis is probably only qualitative, it is clear that less aluminum is detected at the thin line (Figure 4d) than inside the irregularly polygonal-shaped region (Figure 4c). This lower level of aluminum was confirmed at many other locations through the whole scaled region. Figure 4e is another representative image of the scaled region acquired at the marked region in Figure 4a, and shows many lines on the surface. A higher magnification (×50,000) SEM image (Figure 4f) shows that the line is slightly protruding from the surface. It should also be emphasized that the width of the line is almost the same as the width of γ channels in the underlying microstructure (see Figure 5). To investigate the line and surrounding area, SEM–EDX was used and also showed two representative spectra: the spectrum acquired at the point marked “N” was almost the same as that acquired at point “d” in Figure 2b, and the spectrum at point “A” was almost the same as point “c.” This means that less aluminum with nickel and oxygen was detected on the line (point “N”), whereas higher peaks of aluminum with oxygen at “A” were detected. These analyses were also confirmed at many other points along the lines. This result highlights that the scaled region is completely oxidized, which is in good agreement with previous analysis using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The detection of two different morphological regions may explain the iridescence phenomenon on the surface of a turbine blade in the postcast condition. The EDX results also suggest that the presence of different element peaks depending on the analysis points infers the existence of complex oxides in the scaled region.

### 3.2. High-Resolution Observation of the Scaled Region

The previous images, especially Figure 4f, showed that the lines containing nickel and oxygen with lower amounts of aluminum slightly protruded from the surface. To examine the protrusion, a region was selected and carefully cross-sectioned by FIB. As previously stated, there were two different oxidized regions: one is the tessellated region with irregular polygons and the other with...
Figure 4. High-magnification SEM images and SEM–EDX spectra of the surface scale: a) general image, b) magnified image at the marked region in panel (a), c,d) SEM–EDX spectra at the marked points, respectively, in (b), e) magnified image at the marked region in (a), and f) extremely high-magnification image at the marked region in (e).
many lines. Therefore, a specific region containing both of these regions was selected as shown in Figure 5a. To the left of the image there are long lines and the polygonal-shaped oxidized surface, whereas there are a number of fine lines or fine particles to the right. A protective platinum layer was deposited on the central region of Figure 5a and cross-sectioned by FIB (Figure 5b). Figure 5c is a tilting view of the cross-section revealing the thickness of the surface oxide. For detailed investigation, the surface region was observed at higher magnifications (Figure 5d–f) and showed several important findings: 1) The existence of a thin oxide layer (actually double oxide layers; see also Figure 7) with a thickness of about 300–500 nm showing dark contrast between the top Pt layer and the base material, which is much thinner than the initial aluminum oxide of about 2 μm in the unscaled region. 2) The oxide layer looks dense and continuous, which is important to protect the subsurface metal from further oxidation. 3) Beneath the oxide layer, there exist two different microstructures in the base material: one is a quite large γ’ phase and an elongated γ (the left side of Figure 5d,e) and the other is a more normal microstructure composed of thin γ channels and a fine precipitate of the γ’ phase (the right side of Figure 5d,f). 4) In Figure 5e, there are long strands of γ phase in the region with large γ’, which continue into the surface oxide layer and the tip of the γ phase broadens within this oxide. This

![Figure 5. SEM images of cross-sections of the surface scale: a) plain view of a selected region, b) plain view after platinum deposition and cross-sectioning, c) general tilting view of the cross-section in (b), d) close view of the cross-section after increasing contrast, and e,f) magnified images at the marked regions, respectively, in (d). The white arrows in (b) and (d) indicate the protective platinum layer.](image-url)
channels can be seen clearly in the lower phase in the surface oxide is coincident with the slight surface protrusion of the oxide. 2) In Figure 5f, the thin γ channels over the base material showing a more normal microstructure also continue into the surface oxide. And each thin γ channel that continues into the surface oxide is coincident with the slight surface protrusion of the oxide.

To confirm that the protrusion of the surface oxide was due to the oxidation on top of the thin γ channels, the plain view (Figure 5a) and its cross-section (Figure 5d) are compared and shown in Figure 6. The protruding oxides on the surface were matched to the thin γ channels in the cross-section.

To confirm these observations and to undertake a detailed analysis of the oxide, a TEM sample was made exactly from the platinum-deposited region in Figure 5b by an FIB lift-out technique. Figure 7 shows the TEM images and element maps of the scaled region. Even though a platinum layer was deposited on the surface to protect it during TEM sampling, as shown in Figure 7a, the layer was slightly milled away but the top part of the oxide layer survived. It is clear that the TEM image indicates that the oxide layer is a double layer between the Pt layer and the base material: one is the upper oxide layer with the thickness of about 100−200 nm, and the lower oxide layer of thickness about 200−300 nm. The γ channels can be seen clearly in the lower oxide layer but they terminate at the interface between the two oxide layers (Figure 7b). Another TEM image in Figure 7c shows that the upper oxide is dense, whereas the lower one is clearly porous. Chemical analysis of the oxide layers was performed using STEM−EDX: element maps corresponding to the image in Figure 7c indicate that the top oxide layer is mainly composed of nickel, cobalt, and oxygen, while the bottom one is rich in aluminum, chromium, and oxygen. STEM−EDX point analysis confirmed the existence of aluminum and chromium in the top portion of the lower oxide layer not in the upper oxide layer (spectra not shown here). The formation of these complex multioxides is in good agreement with previous results, which used other analysis techniques such as AES and XPS.

3.3. High-Magnification Observation of the Boundary of the Scaled and the Unscaled Regions

It is known that an initial aluminium oxide, which forms through the interaction between mold materials and the melt, remains in place in the unscaled region, as already shown in Figure 2, while complex multioxides are observed in the scaled region. To understand the difference of the scaled region and the unscaled region, their boundary region was also observed. Figure 8 is high-resolution observation of the boundary between the scaled and unscaled regions. The two regions were easily distinguishable due to the different contrast, as shown in Figure 8a (see also Figure 2a). A higher-magnification SEM image (Figure 8b) also shows the boundary region. Due to the typical charging effect of ceramic particles remaining on the surface of the unscaled region, the top half part (the unscaled region) is blurred, whereas the bottom part (the scaled region) is relatively clear, which means that the two regions are composed of different materials or have different thicknesses of oxide(s). A platinum layer was deposited on the central region containing the boundary (Figure 8c). After the deposition, the unscaled region became visible and clear due to the sputtering effect of platinum during deposition by FIB. Then, the region was mechanically rotated in the chamber of an FIB machine and cross-sectioned. Figure 8d shows a low-magnification image after cross-sectioning and confirms that the left portion is the scaled and the right is the unscaled region. The whole cross-section (Figure 8e) shows several interesting features: 1) Along the boundary line of the base material and the oxide in the unscaled region or the Pt layer, it seems that there is oxide-free or extremely thin (about 0.3−0.5 μm) oxide in the scaled region and thick (about 2 μm) oxide in the unscaled region. 2) Even though the thickness of each oxide in each region is different, the oxides in the two different regions, respectively, are continuous. 3) Beneath each surface oxide layer, the microstructure of the base material is continuous without any break at the boundary, which suggests that the microstructure of the base material does not affect the formation of the scaled or unscaled region.

For detailed analysis, the region containing the oxide layer in the unscaled region was further investigated. Figure 9 is an SEM image and SEM−EDX spectra of the oxide layer. First of all, there are many bright particles in the top part. The corresponding SEM−EDX spectrum acquired at point “b” shows that they are zirconium silicate (originally from the mold material) remaining on the top surface of the unscaled region (Figure 9b). Just beneath or surrounding the bright particle, there is a thin layer showing dark contrast, which corresponds to aluminum silicate even though its SEM−EDX spectra were not shown here (but similar results will be shown in Figure 11). Beneath the aluminum silicate layer, there is a gray-colored layer that was marked as “c,” which corresponds to aluminum oxide (Figure 9c). Finally, there is the base material without any oxygen peak.

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Figure 6. Comparison of a selected region before and after cross-sectioning. Note that the arrows indicate the γ channel.
Figure 7. TEM observation and STEM–EDX mapping of the surface scale: a) general image by STEM–HAADF, b) magnified image at the marked region in (a), and c) STEM–HAADF image showing the double oxide layers and corresponding STEM–EDX element maps of nickel, oxygen, platinum, aluminum, cobalt, and chromium. Note that the top protective platinum layer over the γ channels in (a) was slightly milled away during FIB TEM sampling.
It should be emphasized that the aluminum oxide layer is continuous, even though the thickness is slightly different depending on the location, which was also confirmed in other regions. In addition, the SEM image shows an interesting finding that there is a gap between the aluminum oxide and the base material; however, the bottom line of the aluminum oxide and the top line of the base material are well matched, which means that the aluminum layer was stripped off from the base material. In addition, it also means that when the aluminum oxide is stripped off, the fracture occurs between the interface of the oxide/base (not inside the oxide) due to the relatively weak bonding between the metallic base material and the ceramic alumina.

(Figure 9 d). The previous results clearly showed that the initial aluminum oxide that covered the whole surface of a turbine blade was partially removed and multioxides were formed in the scaled region. Therefore, if it is possible to observe the initial oxide layer in the scaled region, it will be crucial to understand the formation mechanism of the scaled region. After thorough and extensive scanning of the whole scaled region in a turbine blade by SEM, a region with evidence of a remnant shell was found (Figure 10a). As already mentioned, the scaled region is not smooth but this shell-containing region was seen to be relatively

3.4. Observation of a Specific Region That Had Been in Contact with the Mold but Remained in a Scaled Region

The previous results clearly showed that the initial aluminum oxide that covered the whole surface of a turbine blade was partially removed and multioxides were formed in the scaled region. Therefore, if it is possible to observe the initial oxide layer in the scaled region, it will be crucial to understand the formation mechanism of the scaled region. After thorough and extensive scanning of the whole scaled region in a turbine blade by SEM, a region with evidence of a remnant shell was found (Figure 10a). As already mentioned, the scaled region is not smooth but this shell-containing region was seen to be relatively
Figure 9. A close SEM image at the marked region in Figure 6e and SEM–EDX spectra at the marked points, respectively, in (a), (b–d).

Figure 10. A specific region containing the initial alumina and mold materials inside the surface scale region: a) general view, b) close view at the marked region in (a), c) SEM–EDX point analysis on the dark contrast region in (b), and d) tilting view after cross-sectioning. The arrows in (b) indicate the points that showed the existence of zirconium peaks by SEM–EDX.
It should be emphasized that this region is located in the middle of the scaled region, far from the boundary between the scaled and unscaled regions. Furthermore, SEM–EDX point analysis (Figure 10c) clearly showed the existence of zirconium (which can only be sourced from the shell mold) in the central dark-contrast region (marked with arrows in Figure 10b), which means that the region had been in contact with the mold and was preserved after casting. Figure 10d shows a tilting view after cross-sectioning by FIB. It seems that there is a layer showing dark contrast between the top protective platinum and the base material. Figure 11 is a higher-magnification SEM image and SEM–EDX spectra acquired at the marked regions in Figure 10d. The higher magnification observation shows that the dark-contrast layer is not continuous but is composed of a number of fine particles of different contrasts (Figure 11a). There are also a number of visible but fine gaps between each particle, which means the layer containing particles is not dense or continuous. Even though the particles are small and there is an inherent interaction volume of sample/beam during analyzing, SEM–EDX analyses indicate the existence of rhenium even though the size of rhenium-rich particles was extremely small (Figure 11e), which is the slowest-diffusing element in the CMSX-10 alloy and also important when understanding the formation mechanism of the surface scale.

4. Discussion

4.1. Formation of Surface Scale by the Interaction of Mold and Melt During Casting

Surface scale is commonly found on the surface of as-cast components. As already shown, extremely thin oxide layers covered the surface of the scaled region, whereas a relatively thick oxide remained in the unscaled region. Before discussing the formation mechanism of the surface scale, it is necessary to understand the two different types of oxides covering the scaled and unscaled regions.

During casting, the melt containing the alloying elements contacts the mold composed of ceramic particles. It is known that there is strong interaction between the elements in the molten metal, particularly, aluminum, and the mold materials, especially silica. As a result, the following reaction is induced

$$4\text{Al}_l + 3\text{SiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Si}_l$$  \hspace{1cm} (1)  

For this reaction, it is also known that the Gibbs free energy has a negative value ($\Delta G = -317 \text{ kJ mol}^{-1}$) for CMSX-10. Therefore, aluminum in the melt forms alumina with the reduction of silica over the liquidus temperature. Then, a thick (about 2 μm) and continuous alumina covers the surface of casting components. However, when casting components are cooling down,
they detach from the mold due to different thermal contraction rates between the metallic casting component and the ceramic mold. A numerical modeling study predicted a gap with the size of about 40 μm between the metal component and the mold.\cite{10} When the separation occurs, the alumina layer on the top surface of the base material can be stripped off from the metal, as already shown in Figure 9, and the detached alumina remains attached to the mold wall. If the alumina layer had formed on pure aluminum or aluminum alloy, the spallation might occur inside the oxide or the metal due to the strong bonds between the oxide and the metal by the ionic component and covalent contribution.\cite{20} However, in this study, the fracture occurred between the alumina and the base material containing many alloying elements due to their relatively weak bond.

After the spallation, the fresh base material is exposed to the atmosphere in the casting furnace. Even though the casting of turbine blades is performed in an industrial vacuum, further oxidation is inevitable in the superalloy containing alloying elements with high oxygen affinity, such as aluminum. It is known that at the oxygen partial pressure exceeding $10^{-40}$ to $10^{-15}$ kPa, aluminum oxide easily forms.\cite{21} As a result, the surface of the newly exposed metal in the scaled region, especially the γ phase due to the strong partitioning behavior of aluminum (Table 1), is easily covered with a thin oxide layer, as shown in Figure 5 and 7. This strong interaction between the base material and the mold, the formation and spallation of an initial alumina layer, and the formation of a new oxide layer result in the formation of the surface scale.

However, this formation mechanism alone cannot explain the reason of the occurrence of the two different regions, scaled and unscaled, on the same turbine blade. In addition, it is difficult to explain the detection of double oxide layers, as shown in Figure 5 and 7. It is also difficult to understand why the scaling phenomenon always occurs in the part of the casting that solidifies last.

The current observation results (Figure 2, 9, and 11) explain why two different regions can form in the same turbine blade. In the unscaled region, the initial alumina layer with the thickness of about 2 μm covers the surface. In addition, the alumina is dense and continuous. If this alumina remains on the surface, the fresh surface of the base material is not exposed and consequently there is not any further oxidation. By comparison, in the scaled region the initial aluminum oxide layer is not dense and continuous due to the extended reaction between the initial alumina and the mold material. As a result, several different types of particles exist and consequently, there is no strong binding between these particles. Therefore, the oxide layer on the top surface of the base material in the scaled region can be easily stripped off when the base material is detached from the mold. After the spallation, there is subsequent oxidation of the bare metal.

The high-resolution observation of the oxide layer formed in the scaled region explains the detection of double oxide layers. The γ channel continued from the base material and terminated near the middle of the newly formed oxide (Figure 5, 6 and 7), implying that there were two different oxidation behaviors. Aluminum and chromium in the alloy have stronger affinity for oxygen than nickel. Consequently, when the base material in the scaled region is exposed to the atmosphere in a furnace, two different oxidation phenomena occur. There is an oxide formed on the surface of the base material made up of nickel and cobalt oxides (Figure 7) and an oxidation of the elements remaining in the base material (aluminum, Figure 7). This oxidation behavior of the base material affects the γ' more than the γ as the γ channels remain in the oxide layer. Due to the loss of elements from this base material region the oxide can be seen to be porous (Figure 7). This phenomenon of retaining the γ channels within the oxide layer may form a composite effect, which makes it difficult to remove the oxide from the scaled region by industrial postprocessing. This is in contrast to the tightly adhered layer of alumina on the surface of the unscaled region of turbine blades, which is easily removed by industrial postprocessing.

Then, the remaining question is the reason for the occurrence of scaling in the region where the casting components solidify last. Within the scaled region there were islands of aluminum silicate adhered to the surface and rhenium-rich particles detected near the surface of the melt in the scaled region (Figure 11). In addition, it should be noted that the scaled region is always found in the portion of the turbine blade that is at the top of the casting and therefore remains hottest for longest. Aluminum is present in the alloy and alumina is found in the shell mold along with silica and zirconium silicate, which means that aluminum silicate did not originally exist but is a product of the casting process. Aluminum silicate, also known as mullite, is made through the reaction of alumina and silica at high temperature and is the only stable intermediate phase in the alumina-silica system at atmosphere pressure.\cite{22} The aluminum silicate was detected between alumina and zircon silicate (Figure 11) and none of the alumina particles seen in this region are large enough to be the stucco applied during shell build, showing that the aluminum silicate in this region was a product of the reaction of the aluminum in the melt and the silica in the shell mold, which means that the scaled region was exposed to high enough temperature for long enough to induce the reaction between alumina and silica. The long times and high temperatures are also confirmed by the detection of rhenium-rich particles near the top surface of the base material (Figure 11). Rhenium is the alloying element with the slowest diffusion rate in Ni-based superalloys. Even compared to tungsten ($4 \times 10^{-15}$ m$^2$ s$^{-1}$ at 1300 °C), the diffusion coefficient ($8 \times 10^{-10}$ m$^2$ s$^{-1}$) of rhenium is several orders of magnitude lower.\cite{23} However, as the scaled region was exposed to high enough temperature for long enough, rhenium atoms could diffuse sufficiently to form the rhenium-rich particles near the surface. As a result of this the top part of the base material where rhenium-rich particles were detected in the scaled region showed a distorted or unstable microstructure (Figure 11), whereas the top part in the unscaled region showed a normal microstructure. The detection of a different set of oxides in the scaled region shows that the alumina that forms elsewhere on the blade has the opportunity to further react with the shell mold materials. This subsequent reaction removes the protection afforded by the alumina and then allows further oxidation of the metal surface but with other constituents of the alloy. Based on these observations and explanations, the formation mechanism of the surface scale is described in Figure 11 and summarized as follows. 1) There is contact of melt to a mold and formation of an initial alumina layer by the reaction of the aluminum in the melt and silica in the mold. 2) In the scaled region, there is further reaction of this alumina layer and the silica in the
shell mold, to form aluminum silicate. 3) This new layer of aluminum silicate, alumina, silica, and zirconium silicate is not retained in place during the initial cooling of the casting revealing a fresh metal surface in the scaled region while retaining the alumina on the surface of the metal in the unscaled region. 4) New oxidation occurs on the metal surface. There is the formation of porous aluminum and chromium oxide and consequently, the lower oxide layer as oxygen penetrates the metal surface in a region with less aluminum. 5) There is further oxidation of nickel and cobalt from the base material by diffusion through the porous lower layer, and consequently, the upper oxide layer.

There have been long-term oxidation studies of Ni-based superalloys, which may suggest a slightly different formation mechanism of the oxidation.[24] After the fresh surface of the metal is exposed, nickel atoms from the base material diffuse out and form the upper nickel oxide layer, and oxygen atoms that existed in the furnace atmosphere diffuse inward and form the bottom aluminum oxide layer. However, based on the TEM observation in Figure 7, it is more difficult to envision the inward diffusion of oxygen through the dense upper nickel oxide layer. This difference may be due to the previous investigations being carried out with long exposure times at high temperatures with an air atmosphere. However, in this study, the oxidation occurred during casting of the component in vacuum, limiting the interaction time to around 2 h. Therefore, the formation mechanisms of these oxides are probably different, but it requires further investigation.

4.2. Prevention of the Formation of Surface Scale

As surface scale is an industrial problem in the casting of single-crystal turbine components, the industrial solution has been to use blasting and surface grinding to remove the scale, which increases the casting cost by around 10% due to rework and scrap. The alumina layer in the unscaled region is easy to remove and is not an issue for the foundry. This is supported by the finding in this study that the fracture or detachment of the oxide occurred between the base material and the oxide/mold (Figure 9). Based on this current study, it is possible to determine a strategy for the prevention of the formation of the surface scale itself.

For the scale to form the following conditions should be satisfied: 1) oxygen partial pressure; 2) high enough temperature in an area of the cast component to allow the shell mold to react with the metal; 3) sufficient exposure of the casting at high temperature to the oxidizing atmosphere. If the time is too short, extremely thin oxides just a few nanometers in size naturally form on the fresh surface.[25] not an oxide of thickness about 300–500 nm as observed in this study.

As turbine blades are cast to a well-established and fixed time and temperature schedule, it is difficult to change the time or temperature in a foundry environment. Therefore, the only approach is to remove or minimize the partial pressure of oxygen in the furnace, or in the development of new face coat materials in the mold, which can reduce the strong reaction between the mold and the liquid metal.[9] This study concluded with an investigation into a turbine blade casting that had been allowed to cool down from the casting temperature in an argon atmosphere. Figure 13a is a general view of a turbine blade that was cooled for a slightly extended period before removal from the furnace and this cooling cycle was done under an argon atmosphere. This atmosphere was introduced after the conclusion of the casting cycle. First, it can be seen that the previously scaled region, which is indicated by an arrow (cf., Figure 1) has a bright contrast similar to the unscaled region (Figure 13a). This bright region was also present on the concave side of the blade. A high-magnification image of the bright-contrast region (Figure 13b), which was acquired exactly at the same magnification as Figure 4b, clearly shows a different surface morphology to that seen in the scaled region. Instead of the tessellated morphology of irregular polygons bordered with a line in the scaled region (Figure 4b), the surface of the bright-contrast region looks like a terrain of steps slightly protruding from the surface (Figure 13b). Importantly, almost no oxygen signal (SEM–EDX) was acquired on the bright-contrast region. A cross-sectional image that was made by the cross-sectioning of the surface inside the bright-contrast region (Figure 13c) clearly shows that there is no notable oxide between the protective platinum layer and the base material. Outside the bright region,
the surface was covered with a thick alumina that remained on the surface, which is a similar result to that with the unscaled region in the blade containing the dark-contrast region (Figure 2). It can be seen that the separation of the oxide layers in the bright region still occurs as had happened under the surface scale but in this case the protective argon atmosphere prevented the formation of any further oxide and surface scale was avoided.

5. Conclusion

The surface scale formed on the surface of as-cast turbine blades was observed by electron microscopy. The surface scale was formed on both the concave and the convex aerofoil of a turbine blade toward the top of the cast part and easily recognized because of the dark contrast. At low magnifications, the scaled region looked smooth but high-magnification observation revealed that it was not smooth and also not a uniform surface layer. The cross-sectional image of the surface scale showed that thin oxide layers, formed after exposing the fresh surface of the base material through the detachment from the shell mold, covered the surface of the scaled region. By comparison, in the unscaled region, the initial alumina layer, which was originally formed by strong interaction between the silica in the mold and aluminum in the melt, remained on the surface of the unscaled region and protected it from further oxidation. The oxide in the unscaled region was quite thick (about 2 μm) and continuous, whereas the oxide in the scaled region was much thinner (about 0.3–0.5 μm) and was composed of double oxide layers: the outer layer being a continuous nickel–cobalt oxide layer and the other a porous aluminum and chromium oxide layer. The microstructure of the base material did not affect the formation of the two different regions—the scaled and unscaled regions—but it affected the oxidation behavior of the fresh surface when exposed to the oxidizing atmosphere. Finally, a turbine blade cast in a modified casting cycle showed the possibility of prevention of the surface scale by preventing further oxidation after exposing the fresh surface of the base material.

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Conflict of Interest

The authors declare no conflict of interest.
Data Availability Statement

Research data are not shared.

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