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Whisker growth morphology of high temperature oxides grown on 304 stainless steel

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ABSTRACT

During the high temperature oxidation of as-cast Type 304 stainless steel there is a complex growth pattern of the oxide layers which is shown to be dependent on; alloy composition and local segregation, surface finish, temperature and atmosphere. Of interest is the appearance of whisker growth morphologies which grow in excess of 10 μm in length and at random orientations to the sample surface. This paper illustrates these features and discusses the formation mechanism in terms of the oxide microstructure.

1. Introduction

Stainless steels are frequently used in high temperature applications due to their excellent toughness, creep properties and corrosion resistance [1]. The exposure of stainless steels to high temperatures, in an oxidising atmosphere, results in the growth of complex oxides on the surface of the metal. Ideally this oxide would be a protective chromia layer which would shield the underlying substrate from further oxidation [2]. At elevated temperatures, however, a multi-layer oxide develops which exhibits complex chemistries, structures and microstructures. The growth of these oxides is a diffusion based process which depends on a number of factors including, the chemical and crystallographic composition of the substrate, the degree of disorder in the substrate (e.g. amount of grain boundaries), the oxidising atmosphere and temperature [3]. A number of recent studies have been successful in characterising these oxide layers using a range of analytical techniques [4–9]. For standard austenitic stainless steels (Types 304 and 316) the oxide consists of a chromium rich spinel layer closest to the substrate, an iron chromium corundum layer and a final thin haematite layer nearest the atmosphere [10]. At higher temperatures or for extended periods of time "breakaway" oxidation has been observed where fast oxidation occurs in localised areas of the metal surface [7,11]. The cause of breakaway oxidation is unclear but observations have linked it to underlying features in the microstructure for example grain boundaries, chemical failure [7] or cracking of the surface due to the build up of stresses within the scale [11].

Breakaway oxidation usually leads to a less protective oxide layer, as iron rich oxides grow above the more protective oxide layers, particularly on stainless steel [7]. Breakaway nodule growth also leads to a more inhomogeneous oxide layer which can be detrimental to the metal in-service and can lead to, for example; interrupted flow of gases, steam or liquids in tube and pipe, or cause localised descaling of components leading to metal thinning and potentially eventual failure.

Generally work on high temperature oxides has concentrated on cross sections to determine oxide features such as thicknesses, and hence growth rates, and microstructural features such as grain size, phase distribution and crystallographic texture [4–7,11,12]. Surface features have been of less interest, however, the surface morphologies of oxides can play a critical role to the materials in-service.

2. Experimental procedure

The substrate material was a Type 304 stainless steel, 18.3 wt.%Cr, 8.10 wt.%Ni, 0.04 wt.%C which had been continuously cast into billet. Small sections of the material were cut to give one side with an area of ~100 mm^2. The surface to be oxidised was prepared metallographically either to a ground finish (240 grit) or to a polished finish (1 μm). The samples were placed in a ceramic boat, with the prepared surface uppermost, and the boat placed in a tube furnace with free flowing air at the set temperature of either 750 °C or 800 °C for time up to 24 h. Following oxidation the samples were removed from the furnace and allowed to air cool to room temperature. The samples were examined using a Leo 1530 VP

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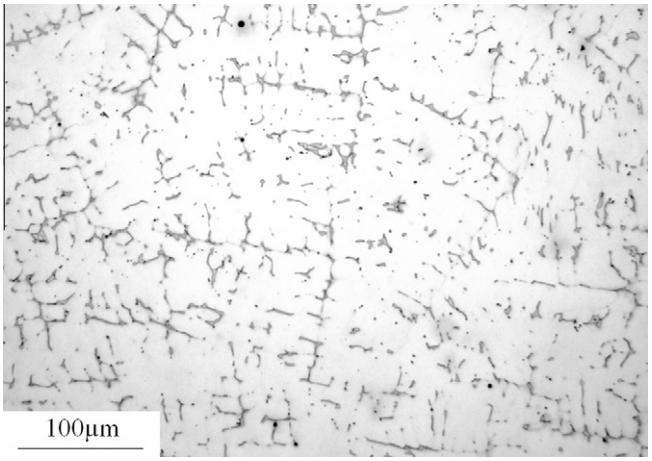

Fig. 1. Optical micrograph of the as-cast microstructure.

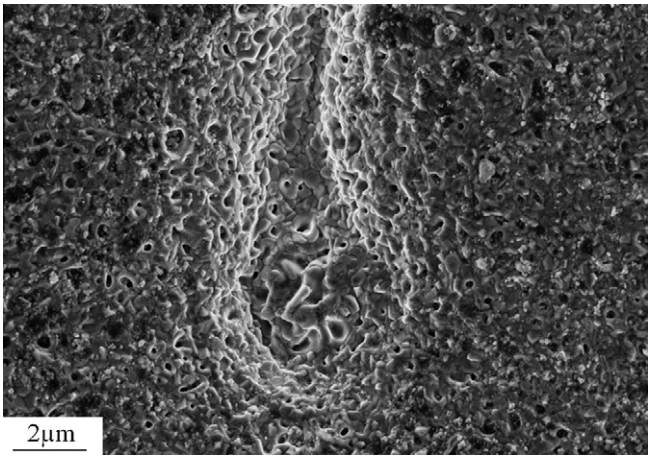

Fig. 3. Electron micrograph of the delta ferrite region of the oxide grown on the polished surface at 800 °C for 24 h.

Field Emission Gun Scanning Electron Microscope (FEG-SEM) with an EDAX Pegasus EDS system which allows both point (spot) analysis and chemical mapping.

3. Results and discussion

Fig. 1 shows the as-received microstructure of the material. The as-cast structure is made up of retained delta ferrite which is present in a predominately vermicular morphology [14] in an austenite matrix. Fig. 2 shows low magnification electron micrographs of the polished and the ground surfaces following oxidation at 750 °C for 4 h. There is a clear difference in the oxidation of the two surface finishes. The ground sample shows a more homogeneous distribution of oxide over the surface with the grinding marks clearly visible. On the polished sample the oxide formed follows the pattern of the microstructure seen in the as-cast structure, Fig. 1. This is due the segregation of chromium to the regions of delta ferrite leading to a localised increase in the oxidation resistance at these positions. The more homogeneous scale on the ground surface is in agreement with the work of Ostwald and Grabke [15], where it was found that working a surface resulted in the formation of faster diffusion paths. Following oxidation for 24 h at 800 °C the polished surface exhibited a similar morphology to that seen at 750 °C with the as-cast microstructure clearly mirrored in the oxide developed on the surface of the samples. A higher magnification electron micrograph of a region containing delta ferrite is shown in Fig. 3. The main body of the oxide appears porous with little structure seen on the surface. Over the regions over the delta ferrite, however, the oxide is more crystalline in nature being made up of small tetrahedra showing the oxide to have a cubic structure

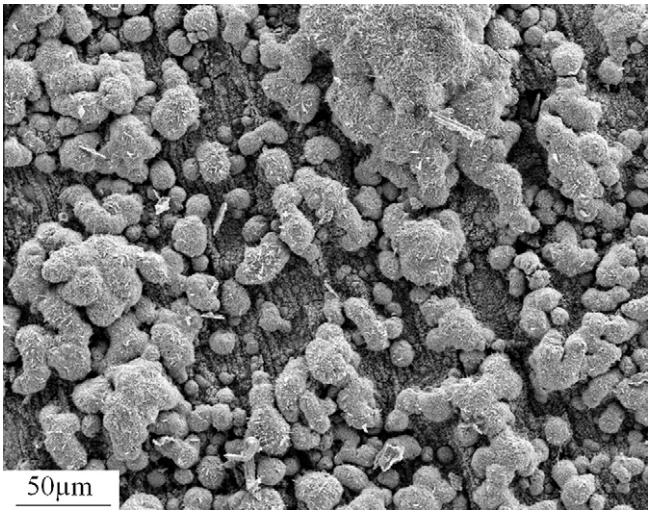

Fig. 4. Electron micrograph of the nodular breakaway oxidation on the on the ground surface at 800 °C for 4 h.

[16]. This tetrahedral structure is more typical of the oxides formed on these steels.

On the ground sample, Fig. 4, at the higher oxidation temperature of 800 °C for 4 h, there were areas of advanced nodule growth which indicates areas of breakaway oxidation [6,7,11]. These nodules were grouped in discrete regions with flatter more homogeneous oxide seen in the inter-nodule regions, Fig. 5. Within these

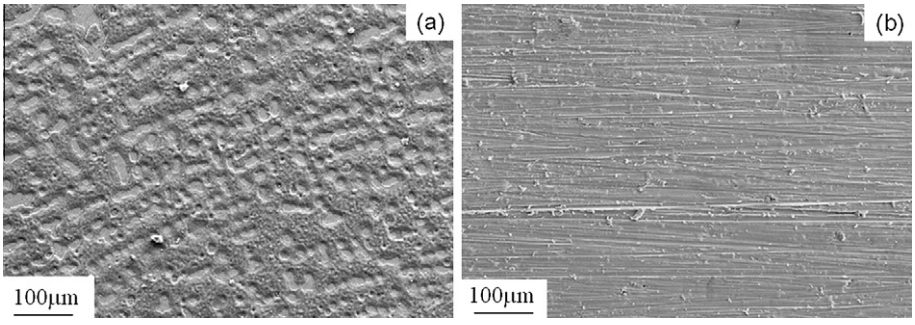

Fig. 2. Electron micrographs of the oxide formed at 750 °C after 4 h (a) on a ground surface and (b) on a polished surface.