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Suzanne Vernier, Eric Andrieu, Lydia Laffont. Flash Oxidation Tests to Evidence the Segregation of Boron at the Grain Boundaries of Superalloy Inconel 718. *Materialia*, 2021, 15, pp.100989. 10.1016/j.mtla.2020.100989 . hal-03109348

HAL Id: hal-03109348

<https://hal.science/hal-03109348>

Submitted on 13 Jan 2021

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Official URL: <https://doi.org/10.1016/j.mtla.2020.100989>

To cite this version:

Vernier, Suzanne  and Andrieu, Eric  and Laffont, Lydia  *Flash Oxidation Tests to Evidence the Segregation of Boron at the Grain Boundaries of Superalloy Inconel 718*. (2021) *Materialia*, 15. 100989. ISSN 2589-1529

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Flash oxidation tests to evidence the segregation of boron at the grain boundaries of superalloy Inconel 718

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ARTICLE INFO

Keywords

Grain boundary segregation
Boron
Borides
Oxidation
Nickel-based superalloy

ABSTRACT

In this study very short oxidation tests, called flash oxidation tests, were carried out at high temperature on samples of superalloy Inconel 718 containing some boron. Following these tests, a specific oxidation pattern was evidenced: spots were observed on the oxide film, these spots being discontinuously distributed along the grain boundaries. Whether outside or inside the spots, the oxide film exhibited the same three oxide layers which were likely rutile oxide (Cr,Nb,TiO_2), chromia oxide Cr_2O_3 and spinel oxide $(\text{Ni,Fe})(\text{Cr,Fe})_2\text{O}_4$. However, inside the spots the oxide film was characterized by thicker oxide layers, a slightly different chemical composition of the spinel layer, and vitreous oxides at the top. Moreover, all the intergranular $(\text{Nb,Mo})_2\text{CrB}_2$ borides of the microstructure were involved in this specific oxidation pattern, thus leading to the suspicion of high boron concentrations within the spots. FEG-EPMA analyses confirmed that, during the oxidation process, boron atoms diffused from the matrix to the oxide film, especially within the spots. Actually, the spots revealed areas where boron was highly concentrated just before oxidation. Such areas originated from the non-equilibrium segregation of boron near grain boundaries, which is a classical phenomenon when cooling and/or reheating a boron-containing alloy. Thus, the spots of the oxide film highlighted the grain boundary segments where boron segregated the most, confirming that the segregation of boron was not uniform within the grain boundary network.

1. Introduction

In the aerospace and power generation industries, the nickel based superalloy Inconel 718 is commonly used for parts which require a high mechanical strength at high temperature (typically critical rotating parts in turbojet engines [1]). Some boron is often added to the chemical compositions of the nickel based superalloys because boron improves the strength and the ductility of the alloys [2–5]. The positive effects of boron arise from the segregation of this element at grain boundaries [6,7], this segregation leading to a change in the grain boundary properties. In literature, several mechanisms have been proposed to explain the effect of boron on grain boundaries. Most often, boron is said to increase the grain boundary cohesion [2,3,5]. But other explanations have been suggested, for instance: (i) boron clusters could act as obstacles to the dislocation movements thus influencing the cracking mode of the alloys [3], (ii) the formation of B vacancy complexes at grain boundaries may reduce the grain boundary diffusion reactions thus preventing the formation of cavities [3]. Alternatively, Kontis et al. [4] showed that adding boron in superalloy STAL15 CC led to the serration of the grain boundaries. Yet, grain boundary serration delays the coalescence of the cavities which form at grain boundaries, while for a flat grain boundary a continuous crack path forms more easily [4]. Non uniform lattice

strains caused by a non uniform segregation of boron along the grain boundaries could explain the grain boundary serration observed when adding boron in superalloy STAL15 CC [4].

If small boron additions are beneficial for the mechanical properties of the alloys, several studies showed that increased boron concentrations led to higher oxidation rates [8,9]. Such degradation in oxidation resistance has been attributed to the fact that boron affects the composition of the oxide scale [8,9]. Indeed, Binder et al. [8] evidenced that increasing the boron concentration in Cr Ni Co Fe alloys accelerated the development of complex spinels at the expense of the more protective oxide Cr_2O_3 . Similarly, Barrett et al. [9] concluded for nickel based superalloys that boron favored the formation of NiO oxide at the expense of the more protective Al_2O_3 and aluminate spinel oxides. Moreover, several studies evidenced boron oxides in the oxide scale of nickel based alloys: CrBO_3 [10,11], Al_3BO_6 [10], $\text{Al}_4\text{B}_2\text{O}_9$ [12] and $\text{Ni}_2\text{CrO}_2(\text{BO}_3)$ [11]. Boron is incorporated in the oxide scale for two main reasons: the high thermodynamic stability of the boron oxides and the high diffusivity of boron in nickel [11] (the boron diffusivity in nickel is between 3 and 4 orders of magnitude higher than that of Ni, Cr or Al [10]). Then, the diffusion of boron towards the oxide scale can largely deplete the bulk alloy from boron, thus degrading the mechanical properties. Indeed, Nowak et al. [10] measured that, after 20 h of oxidation in air at

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Table 1
Chemical composition given in the alloy certificate. Wt. %.

Ni	Fe	Cr	Nb	Mo	Ti	Al
52.39-52.42	19.17-19.18	18.21-18.22	5.18-5.25	3.04-3.05	0.97-0.98	0.50-0.51
Si	Mn	C	Ta	Co	Cu	N
0.07	0.04	0.036	0.01	0.01	<0.01-0.01	0.0040-0.0045
B	P	S	Mg	Ca	Zn	Sn
0.0037-0.0039	0.003	0.0010-0.0011	0.0004-0.0005	<0.0002-0.0002	<0.0010	<0.0010
O	Pb	Ag	Se	Bi		
<0.0010	<0.0003	<0.0002	<0.0001	<0.00003		

1050 °C, 90 % of the initial boron content had left a 2 mm thick sample of alloy Rene 80. Nevertheless, Nowak et al. [10] also evidenced that the oxidation induced boron depletion largely depended on the products of oxidation and so on the alloy composition: the formation of a continuous alumina sub layer suppressed the oxidation of boron and consequently its diffusion towards the oxide scale.

The addition of boron in nickel based superalloys can also lead to the precipitation of borides at grain boundaries [13–17]. The oxidation products of borides depend on the oxidation temperature [18–21]. In deed, when oxidizing such high boron compounds, boron reacts with oxygen to form the oxide B_2O_3 , which is thermodynamically less stable than Al_2O_3 but more stable than Cr_2O_3 [11]. Yet, at atmospheric pressure, B_2O_3 undergoes two phase transformations in the 400 °C–1100 °C range: the solid oxide B_2O_3 becomes liquid between 455 °C–475 °C [22] and around 1000 °C the liquid oxide B_2O_3 starts vaporizing [18–20]. Furthermore, when oxidizing the CrB_2 phase it was pointed out that B_2O_3 can react with Cr_2O_3 to form $CrBO_3$. Murthy et al. [19] reported the oxide $CrBO_3$ in the 800 °C–1000 °C range, while Emiliani et al. [21] reported the oxide $CrBO_3$ at 1100 °C. The $CrBO_3$ oxide is liquid above 855 °C and also decomposes in the volatile oxides Cr_2O_3 and B_2O_3 above 1200 °C [19]. The oxides which liquefy at high temperature can hardly be evidenced on XRD patterns [19] but they have a characteristic appearance: they appear as vitreous phases once solidified [18,19,21].

The objective of the present study was to show that oxidation experiments can be used as a characterization technique which highlights some chemical segregations in the microstructure. The material selected for this study was superalloy Inconel 718. Here the alloy contained some boron but still within the limit imposed by the AMS specifications. Before oxidation the material had been solution treated at 1050 °C (thus above the δ solvus) and that for several durations. A previous work [14] had shown that this material exhibited several phases at grain boundaries: $(Nb,Mo)_2CrB_2$ borides (which had precipitated during a prior subsolvus δ treatment), eventually some residual δ precipitates, and secondary $(Nb,Ti)C$ carbides. But because the material had been previously solution treated at high temperature, large amounts of chemical species were still in solution in the microstructure. Yet, in superalloy Inconel 718, several species are known to segregate at grain boundaries, especially niobium [23], molybdenum [24], carbon [7,24], boron [7,16,24], sulfur [25] and phosphorus [7,24]. The idea was to get some of these segregated species to react with oxygen so as to form specific oxides where chemical segregations were high. To this end, “flash oxidation tests”, which were oxidation tests of typically 1 minute long, were carried out at high temperature. Two reasons explained the choice of such short oxidation times. First, the phases should not have time to evolve during oxidation: during the oxidation tests the segregated species should be involved in the oxide film and not in precipitates. Second, very short oxidation tests should prevent the Cr_2O_3 scale from growing too much and thus from hiding the oxides of interest. Indeed, the oxide Cr_2O_3 is known to be the predominant steady state oxide of superalloy Inconel 718 [26]. Finally, the fast reaction of the segregated species with oxygen also required a high oxidation temperature, and that was why the flash oxidation tests were carried out at about 1050 °C. After performing such high temperature flash oxidation tests on the stud-

ied material, a specific oxidation pattern was evidenced: spots were observed on the oxide film, these spots being discontinuously distributed along the grain boundaries. The origin of such oxidation pattern has been investigated in the present paper.

2. Materials and methods

2.1. Material and microstructure

The alloy studied here was the same cast and wrought alloy as that studied in [14]. Its chemical composition, which is reminded in Table 1, fell within the AMS specifications for superalloy Inconel 718. In particular, the boron content (0.0038 wt.%) was well below the maximum tolerance of the specifications (0.006 wt.%). According to ThermoCalc calculations (TCNI7 database), the δ solvus of the alloy was about 1044 °C.

The flash oxidation experiments of the present study were performed on samples which had been solution treated at 1050 °C (air cooling) after a prior subsolvus δ treatment [14]. More precisely, four types of samples corresponding to four durations of solution treatment were oxidized: ST 10 (solution treated for 10 min), ST 30 (solution treated for 30 min), ST 60 (solution treated for 60 min) and ST 120 (solution treated for 120 min). According to the study presented in [14], the ST 10 type samples mainly exhibited δ precipitates and $(Nb,Mo)_2CrB_2$ borides at grain boundaries (Fig. 1.a), whereas the ST 30, ST 60 and ST 120 type samples only exhibited secondary $(Nb,Ti)C$ carbides and $(Nb,Mo)_2CrB_2$ borides at grain boundaries (Fig. 1.b c). In addition to these intergranular phases, primary $(Nb,Ti)C$ carbides, primary $(Ti,Nb)(C,N)$ carbonitrides and intragranular secondary $(Nb,Ti)C$ carbides could be also noticed [14].

2.2. Method for the flash oxidation tests

The flash oxidation tests were performed under ambient static air in a muffle furnace. The temperature of the muffle furnace was set at 1050 °C, thus above the δ solvus temperature. Before oxidation, the samples were mirror polished using: silica papers (P600, P1200), diamond suspensions containing particles down to 1 micron large and an alumina colloidal solution containing 50 nm large particles. To determine a suitable duration for the flash oxidation tests, an interrupted oxidation test was performed first: an ST 30 type sample was successively oxidized for 0.5 min, 1 min and 1.5 min. Here, the oxidation time was not defined as the time the sample effectively spent at 1050 °C but as the time spent between the furnace closing (introduction of the sample) and the furnace opening (removal of the sample). Thus, the oxidation tests performed in the present study were clearly not isothermal. After the sequence 0.5 min + 1 min + 1.5 min, an interesting oxidation pattern was observed: the bright field optical micrographs revealed brown spots along some grain boundaries segments (yellow arrows in Fig. 2.a). The change in the oxide color from gray/blue to brown indicated that within the spots the oxide film did not have the same optical properties as around. Then, the same spots along grain boundaries were also observed when ST 30, ST 10, ST 60 and ST 120 type samples were oxidized at one time for 1.5 min (yellow arrows in Fig. 2.b).

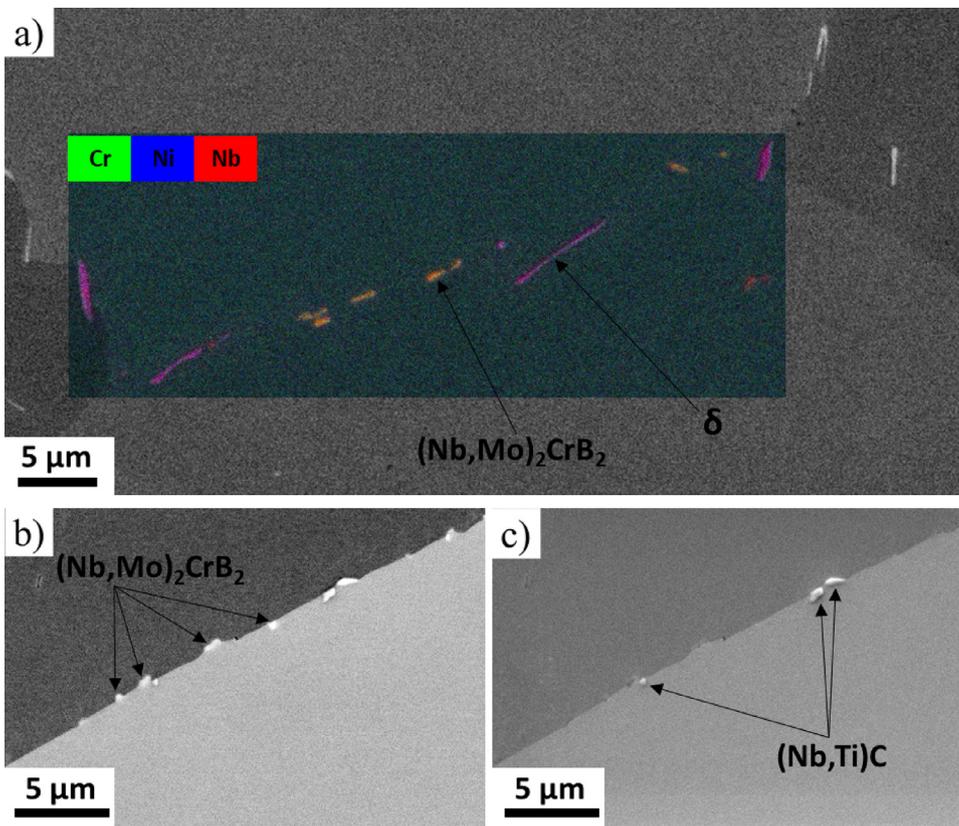


Fig. 1. Microstructure before the flash oxidation tests. a) Sample solution-treated at 1050 °C for 10 min (ST-10 type sample), BSE image and EDS map (10 kV) overlapped. The grain boundaries exhibit both δ precipitates (purple particles) and $(\text{Nb,Mo})_2\text{CrB}_2$ borides (orange particles). b) and c): Sample solution-treated at 1050 °C for 30 min (ST-30 type sample). b) BSE image. c) SE image. The grain boundary exhibits both secondary $(\text{Nb,Ti})\text{C}$ carbides and $(\text{Nb,Mo})_2\text{CrB}_2$ borides. Contrary to the $(\text{Nb,Mo})_2\text{CrB}_2$ borides, the $(\text{Nb,Ti})\text{C}$ carbides are super bright in SE images because they are in relief at the sample surface. For more details on the phase identification the readers are invited to see [14].

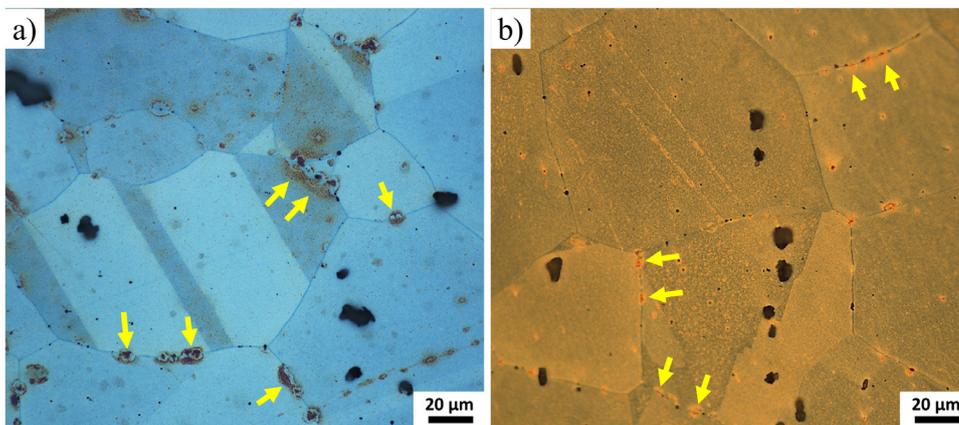


Fig. 2. Overview of the microstructure after the flash oxidation tests. RH-30 type samples, bright field optical micrographs. a) Interrupted oxidation test of 0.5 min + 1 min + 1.5 min. b) Oxidation test of 1.5 min at one time. The yellow arrows highlight brown spots along some grain boundary segments. These spots correspond to areas where the oxide film has different optical properties.

2.3. Characterization techniques

The surface of the oxidized samples were observed in a JEOL JSM 7800F Prime Field Emission Gun Scanning Electron Microscope (FEG SEM). This microscope was equipped with an X Max Silicon Drift EDS detector from the Oxford Instruments Company. To analyze the oxide film on a cross sectional view, cross sectional thin foils were lifted out in a FEI HELIOS 600i Focused Ion Beam Scanning Electron Microscope (FIB SEM). These thin foils were characterized using Transmission Electron Microscopy (TEM). Scanning Transmission Electron Microscopy (STEM) observations and STEM Energy Dispersive X ray Spectroscopy (EDX) analyses were performed in a JEOL cold FEG JEM ARM200F TEM microscope operated at 200 kV. This TEM microscope was equipped with a probe Cs corrector (resolution: 0.78 Å) and with a JEOL CEN TURIO Silicon Drift EDS detector. TEM EDX maps were performed at 200 kV in a JEOL JEM 2100F TEM microscope equipped with a Silicon Drift EDS detector from the Bruker Company.

Both boron and carbon were systematically omitted from the EDX quantifications since they could not be properly quantified based on the present EDX analyses. In fact, the contamination of the sample surface led to incorrect carbon measurements [14]. Then, quantifying boron with the EDX technique should have required low accelerating voltages (as low as 2.5 kV [27]) given that the K_α line of boron is at 0.183 keV, making complicated the quantification of the other elements (Ni, Fe, Cr, Ti, O...). In addition, superalloy Inconel 718 contains both niobium and molybdenum whose $M_{\gamma 2}$ lines (at 0.172 keV and 0.193 keV respectively) are very close to the K_α line of boron, so that the deconvolution of these three lines from an EDX spectrum is very difficult. This way, in the present study boron was quantified on bulk samples using a CAMECA SXFive FE Electron Probe Microanalyzer (FEG EPMA). The FEG EPMA analyses were performed at 10 kV and under 22–26 nA.

Finally, complementary EDS EBSD analyses were performed in a JEOL JSM 7100TTL LV FEG SEM equipped with an X Max Silicon Drift EDS detector and an AZtec HKL Advanced Nordlys Nano EBSD detector,

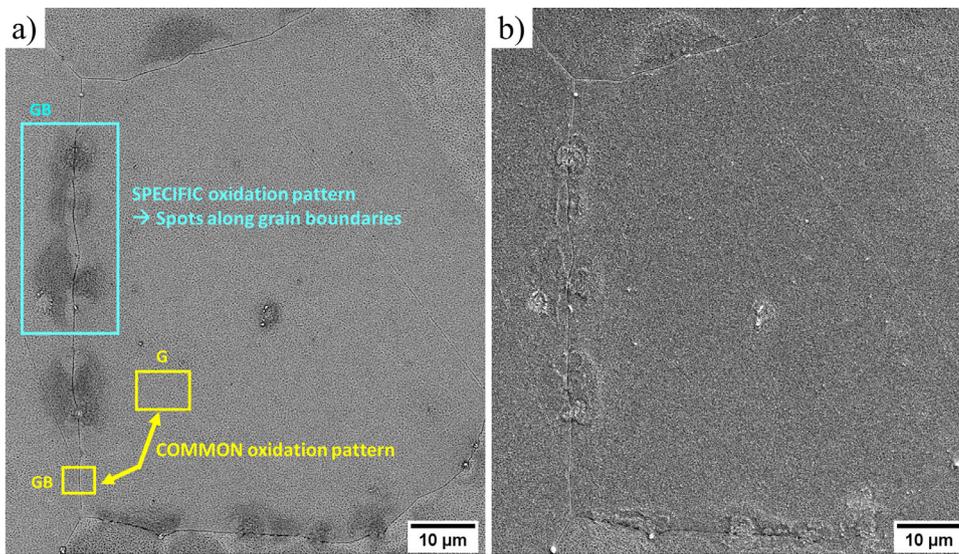


Fig. 3. Oxidation patterns observed in scanning electron microscopy. ST-30 type sample oxidized for 0.5 min + 1 min + 1.5 min. a) BSE image. “GB” stands for grain boundary and “G” stands for grain. The blue rectangle highlights the oxidation pattern investigated in the present study and which appears as spots along grain boundaries. The yellow rectangles highlight common oxidation patterns for both the grain boundaries and the grains. b) Corresponding SE image. The dark spots observed along grain boundaries correspond to areas where the oxide film is locally thicker.

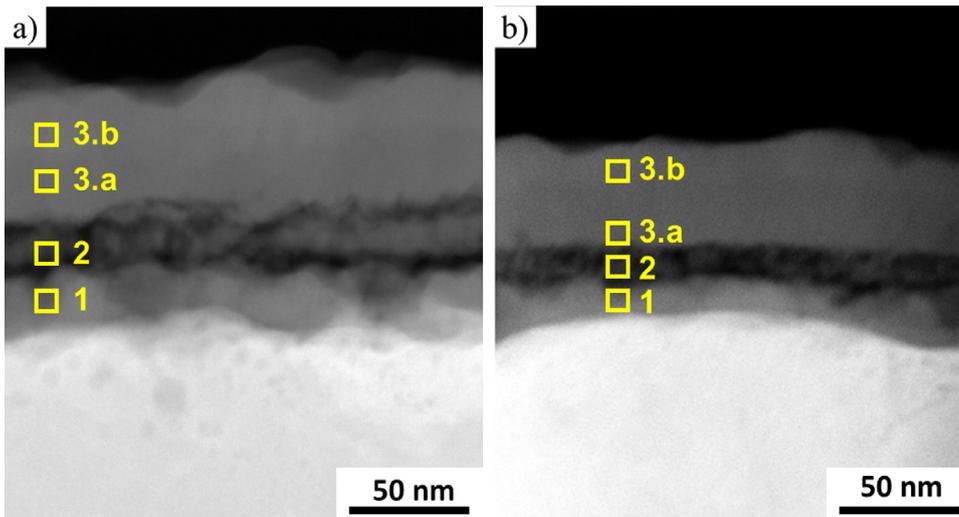


Fig. 4. Cross-sectional view of the oxide film outside the spots. TEM thin-foils, HAADF STEM images. a) ST-30 type sample oxidized for 0.5 min + 1 min + 1.5 min. b) ST-10 type sample oxidized for 1.5 min at one time. Despite different thicknesses, the oxide films of the two samples display the same three layers. The chemical compositions measured in the yellow boxes by STEM-EDX are presented in [Table 2](#).

both from the Oxford Instruments Company. The EBSD data were post processed using MTEX, a free and open source MATLAB toolbox for the analysis of EBSD data [28]. All the characterization devices just mentioned here belonged to the UMS Raimond Castaing (Toulouse, France).

3. Results and discussions

3.1. Products of oxidation out of the spots

The specific oxidation pattern pointed out in optical micrographs (Fig. 2) was also visible in BSE images: dark spots were discontinuously observed along grain boundaries (blue rectangle in Fig. 3.a). The SE images evidenced that the spots coincided with an increased thickness of the oxide film (Fig. 3.b). This meant that the oxidation mechanism was somewhat different in these areas. To properly understand the specificities of the spots, the oxidation products formed out of the spots, both at the grain boundaries and at the grain surfaces (yellow rectangles in Fig. 3.a), must be analyzed first.

Outside the spots, the grains were covered with an oxide film of uniform thickness. The thickness of the oxide film was larger in the case of the interrupted oxidation test (0.5 min + 1 min + 1.5 min) because the temperature exposure had been longer than for the oxidation test performed for 1.5 min at one time (Fig. 4). But, whatever the nature of the oxidation test, outside the spots the oxide film always exhibited the

same three oxide layers (Fig. 4 and Table 2). The oxide layer in contact with the alloy (layer 1 in Fig. 4) was rich in chromium and niobium. It also contained significant amounts of titanium. The oxide layer located above (layer 2 in Fig. 4) was very rich in chromium. Lastly, the top oxide layer (layer 3 in Fig. 4) was rich in nickel, chromium and iron. Furthermore, a chemical gradient was observed through the oxide layer 3: when going towards the air/oxide interface more and more iron (respectively less and less chromium) was measured. Grazing incidence XRD analyses performed after flash oxidation evidenced a spinel oxide and the matrix (γ). This way, the oxide layer 3 was thought to be the spinel oxide $(\text{Ni,Fe})(\text{Cr,Fe})_2\text{O}_4$. Then, some literature results could give indications on the nature of oxide layers 1 and 2. Indeed, after oxidizing samples of superalloy Inconel 625 at 1050 °C, Ramenatte et al. [29] evidenced the rutile oxide $\text{Nb}_{1.5}\text{Cr}_{0.5}\text{O}_4$ at the alloy/oxide interface, just below the Cr_2O_3 oxide scale. Hence, here the oxide layer 1 was likely $(\text{Cr,Nb,Ti})\text{O}_2$ rutile oxide and the layer 2 was likely Cr_2O_3 oxide. Finally, one could notice some fluctuations in the chemistry of the oxide layers. These fluctuations were attributed to the transient nature of the oxides given that the steady state oxidation regime was not reached during such short oxidation tests [30].

The analysis of a grain boundary out of the spots showed intergranular oxidation (Fig. 5). Indeed, three oxides layers A, B and C had penetrated the top of the grain boundary. Deeper, two other oxides, one rich in chromium and one rich in titanium and aluminum, were found

Table 2

Chemical composition of the oxide film outside the spots. ST-30 type sample oxidized for 0.5 min + 1 min + 1.5 min and ST-10 type sample oxidized for 1.5 min at one time. STEM-EDX measurements performed at 200 kV, normalized at. %, carbon and boron were omitted from the quantifications. The oxide film is made of three oxide layers (1, 2 and 3). The oxide layer 3 shows a gradient in chemical composition (see 3.a and 3.b).

Sample	Oxide layer	O	Ni	Fe	Cr	Nb	Mo	Ti	Al
ST-30 type sample oxidized for 0.5 min + 1 min + 1.5 min	1	53.9	5.3	1.9	10.9	22.8	0.0	4.2	1.0
	2	46.0	10.3	3.7	38.8	0.0	0.0	0.8	0.4
	3.a	39.9	20.0	25.8	13.7	0.0	0.0	0.1	0.5
	3.b	39.5	19.7	33.3	7.3	0.0	0.0	0.0	0.2
ST-10 type sample oxidized for 1.5 min at one time	1	62.3	1.0	1.3	12.1	19.1	0.2	3.2	0.9
	2	63.1	3.3	3.0	24.9	3.2	0.3	0.6	1.6
	3.a	59.0	10.3	3.3	26.7	0.0	0.0	0.2	0.4
	3.b	55.6	14.3	22.2	7.4	0.0	0.2	0.1	0.2

Table 3

Chemical compositions measured on several oxidized features. The locations of the measurements are displayed in Fig. 6.b. and Fig. 6.d. EDS measurements performed at 10 kV, normalized at. %, carbon and boron were omitted from the quantifications. Given the spatial resolution of the EDS technique [33] and the small size of the features which were pointed at, the measurements were certainly influenced by the chemical composition of the surrounding areas. Nevertheless, the aim of these EDS measurements was to provide some chemical information for comparing the oxidized features with each other. “GB” stands for grain boundary.

Label	Oxidized feature	O	Ni	Fe	Cr	Nb	Mo	Ti	Al
1	GB without oxide bulges	54.4	10.7	7.5	19.3	4.2	1.4	1.3	1.2
2	GB with oxide bulges	49.6	18.0	6.2	14.4	6.9	3.6	0.8	0.5
3	δ precipitate	51.1	30.2	5.8	3.4	7.9	0.2	1.1	0.3
4	(Nb,Mo) ₂ CrB ₂ boride	51.9	15.1	4.9	13.4	8.2	5.4	0.8	0.4
5	Secondary (Nb,Ti)C carbide	68.7	3.1	4.0	2.3	19.0	0.2	2.5	0.2

(Fig. 5.d). The three oxide layers A, B and C seemed to have the same chemical composition as the three oxide layers 1, 2 and 3 grown over the γ grains (Fig. 4 and Table 2). Intergranular oxidation originates from the diffusion of oxygen inside the grain boundaries and such phenomenon is common when oxidizing superalloy Inconel 718 [26]. However, in the case of superalloy Inconel 718, titanium and aluminum oxides are usually expected inside the grain boundaries [26,31]. Thus, the oxide layers A, B and C and the Cr rich oxide found here were likely to be transient oxides.

3.2. Products of oxidation inside the spots

The oxidation pattern investigated in the present study was found around some grain boundary segments. Yet, before oxidation, the grain boundaries of the material exhibited several phases: secondary (Nb,Ti)C carbides, (Nb,Mo)₂CrB₂ borides and potentially δ precipitates (see Part 2.1). Thus, a connection between the spots and the intergranular phases was examined.

The appearance of the intergranular phases was modified by the oxidation process (Fig. 6) and EDS analyses (Table 3) were used to properly identify them in SE images. The secondary (Nb,Ti)C carbides, whose oxide was rich in niobium (#5 in Table 3), were easily recognizable in SE images because their oxidation led to large volume expansions and “burst” morphologies (Fig. 6.c,d) [32]. On the contrary, the (Nb,Mo)₂CrB₂ borides, whose oxide is rich in chromium, niobium and molybdenum (#4 in Table 3) were totally etched by the oxidation process (Fig. 6.b,d). In addition, oxide bulges with protruding crystallites of oxide (insert in Fig. 6.b) surrounded the oxidized (Nb,Mo)₂CrB₂ borides. Finally, the appearance of the oxidized δ precipitates, which were rich in nickel and niobium (#3 in Table 3), was more uneven: the boundaries of the former δ precipitates were etched by the oxidation process but some oxide could make the center of the oxidized precipitates domed (Fig. 6.b). From this phase identification, it resulted that very few δ precipitates and secondary (Nb,Ti)C carbides were observed inside the spots (Fig. 6). On the contrary, all the borides were involved in a spot (Fig. 6). This suggested a relationship between the spots and the boride

precipitation sites. Besides, within the spots one could also notice grain boundary segments surrounded by oxide bulges with protruding crystal lites, although no (Nb,Mo)₂CrB₂ borides could be observed between the bulges (#2 in Fig. 6.b). Like the oxidized borides, such grain boundary segments were found enriched with niobium and molybdenum (#2 in Table 3). By comparison, the grain boundaries segments without oxide bulges (inside or outside the spots) showed less niobium and molybdenum but more aluminum and titanium (#1 in Table 3), suggesting a mechanism of intergranular oxidation similar to that presented in Fig. 5. The grain boundary segments with oxide bulges were presumed to be boride precipitation sites.

After flash oxidation the (Nb,Mo)₂CrB₂ borides were systematically involved in a spot. Yet, contrary to the δ and (Nb,Ti)C phases, the (Nb,Mo)₂CrB₂ phase contains boron and molybdenum, so that the spots could originate from a local segregation in molybdenum or in boron. In addition, since both boron and molybdenum are known to increase the oxidation kinetics [8], this could explain an increased oxide thickness inside the spots. The segregation of molybdenum was investigated based on STEM EDX and TEM EDX analyses performed on a thin foil cut across a spot (Fig. 7). The thin foil included one of the oxidized (Nb,Mo)₂CrB₂ borides found in the spot (Fig. 7.a,b). As a reminder, boron could not be properly detected with such high energy EDX analyses (200 kV). The EDX analyses (Fig. 7.c) revealed within the spot the same 3 oxide layers as those observed out of the spots (Fig. 4 and Fig. 5): likely (Cr,Nb,Ti)O₂, Cr₂O₃ and (Ni,Fe)(Cr,Fe)₂O₄ oxides. Thus, within the spots the increased thickness of the oxide film originated from an increased thickness of the oxide layers 1, 2 and 3. For instance, in the case of the thin foil presented in Fig. 7, the oxide layers 1, 2 and 3 were respectively 48 nm, 45 nm and 93 nm thick close to the center of the spot (just behind the oxide bulge at grain boundary) while they were respectively 22 nm, 22 nm and 64 nm thick outside the spot. Finally, compared to out of the spots, within the spot the spinel layer was found enriched with iron and depleted of chromium (Fig. 8).

The cross section of the spot in Fig. 7 only showed some molybdenum segregation near the oxidized boride. Indeed, the oxide layer and the matrix located just below the oxidized boride were enriched with

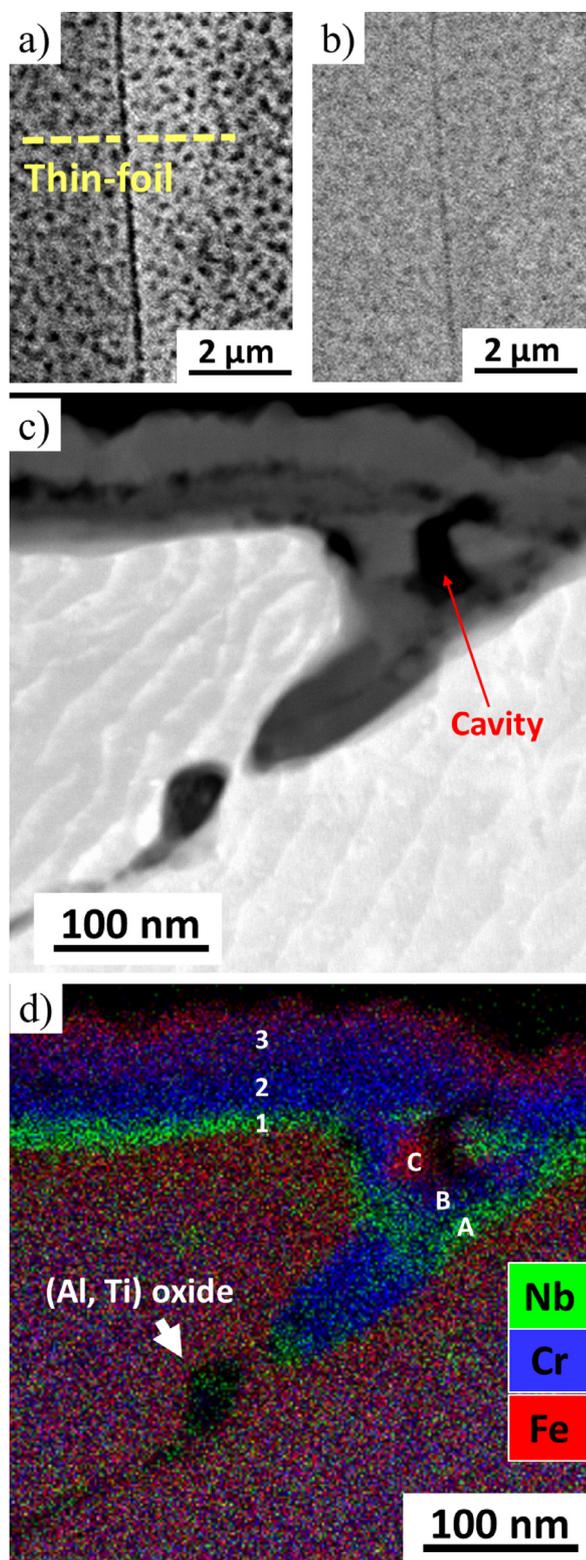


Fig. 5. Oxidation of a grain boundary out of the spots. ST-30 type sample oxidized for 0.5 min + 1 min + 1.5 min. a) BSE image, a thin-foil lift-out was performed across the grain boundary following the dotted line. b) SE image. c) HAADF STEM image of the thin-foil positioned in a). d) STEM-EDX elemental map acquired at 200 kV. Three oxide layers A, B and C are identified inside the grain boundary. These three oxide layers seems similar to the three oxide layers 1, 2 and 3 observed on the γ grains. The white arrow highlights an intergranular oxide rich in aluminum and titanium whose precise composition is 55.60 – 24.9Al – 10.2Ti – 4.7Nb – 2.2Cr – 1.4Ni – 0.5Fe – 0.5Mo at.%.

niobium and molybdenum (Fig. 9.c d). These niobium and molybdenum atoms actually came from another $(\text{Nb},\text{Mo})_2\text{CrB}_2$ boride located right next (Fig. 7.b). This neighboring boride was deep enough so as not to be oxidized itself. However, during the oxidation process some of its Cr, Nb and Mo atoms had diffused towards the sample surface to react with oxygen. Many of the diffusing Cr atoms were incorporated in the upper oxide layers, leading to a Cr depletion in the matrix (Fig. 9.b). On the other hand, some of the diffusing Nb and Mo atoms were incorporated in the inner oxide layer below the oxidized boride (region I in Fig. 9.a), thus leading to oxide crystals with high Nb and/or Mo contents (Fig. 9.c d, the Nb and Mo concentrations could vary strongly in this area). The oxidized boride (regions II and III in Fig. 9.a), which was separated from the inner oxide layer (region I) by a cavity, presented some molybdenum (Fig. 9.c,e). Actually, the base region of the oxidized boride (region II) could be the $(\text{Nb},\text{Cr},\text{Mo})\text{O}_2$ rutile oxide evidenced by Goldschmidt et al. [34] when oxidizing Cr Nb Mo ternary systems. However, the decrease in Mo concentration across the region II evidenced that some Mo of the initial boride had volatilized during the oxidation process, probably as $\text{MoO}_3(\text{g})$ oxide [35]. Indeed, at atmospheric pressure, MoO_3 sublimates from 538 °C to 795 °C, liquefies from 795 °C to 938 °C, and finally evaporates again from 938 °C [35]. In literature some studies attribute the enhanced oxidation rate of the Mo containing alloys to the formation of the volatile $\text{MoO}_3(\text{g})$ oxide. Indeed, the formation of such gas generates pores or cracks in the oxide scale and so makes the oxide scale much less protective [34,36]. Yet, here inside the spots the oxide film did not appear noticeably more porous or cracked than outside the spots. Especially, the outer spinel layer was always found very compact. Some authors also reported the catastrophic oxidation of Mo containing alloys caused by the formation of liquid oxides ($\text{MoO}_3(\text{l})$ and eutectics involving MoO_3) [35,36]. But here no Mo rich layer suggesting the formation of a liquid Mo based oxide inside the spots was observed (Fig. 7.c). Thus, if some Mo enrichment could be noticed very locally at the center of the spots, the spot were unlikely to originate from the segregation of Mo around the grain boundary.

The examination of the top of the oxide film (Fig. 10) provided the first arguments for a boron enrichment inside the spots. Indeed, in SE images, the top of the oxide film appeared mat and smooth outside the spots (Fig. 10.a), while it appeared gleaming inside the spots (Fig. 10.d,f). Yet, Binder et al. [8] had already noticed that the oxide scales of alloys with a high boron content had a “wet” appearance, while the oxide scales of boron free alloys had a “dry” appearance. Thus, the gleaming appearance of the oxide film inside the spots could originate from a high boron concentration in these areas before oxidation. In addition, within the spots, the oxide film exhibited protruding crystallites of oxide (Fig. 10.d,f), similar to those observed on the oxide bulges around the oxidized borides (Fig. 6), and vitreous zones (see yellow arrows in Fig. 10.d,f). The vitreous zones looked like those evidenced by Murthy et al. [19] when oxidizing the composite $\text{TiB}_2 + 10\%\text{CrB}_2$ at 1000 °C. According to Murthy et al. [19], such vitreous zones result from the coagulation of droplets of liquid oxide, either CrBO_3 or B_2O_3 in Murthy’s study. This way, it seemed that during the oxidation process a liquid boron rich oxide formed at the top of the oxide film within the spots. Here, the boron rich liquid phase could hardly be CrBO_3 since no chromium or any metallic enrichment was noticed at the top of the oxide film (Fig. 7). Thus, here there were only two possibilities for a liquid boron rich oxide: (i) pure B_2O_3 , (ii) an oxide rich in iron, nickel, chromium and boron, so that the oxide was mistaken with the spinel oxide $(\text{Ni},\text{Fe})(\text{Cr},\text{Fe})_2\text{O}_4$ during the EDX analyses. Indeed, Jalowicka et al. [11] evidenced the transient oxide $\text{Ni}_2\text{CrO}_2(\text{BO}_3)$ at the top of the oxide scale of the nickel based alloy Rene 80.

3.3. Non equilibrium segregation of boron revealed by oxidation

To quantify boron in the microstructure, FEG EPMA analyses were performed both before (Fig. 11) and after flash oxidation (Fig. 12). The measurements performed before oxidation sometimes seemed to

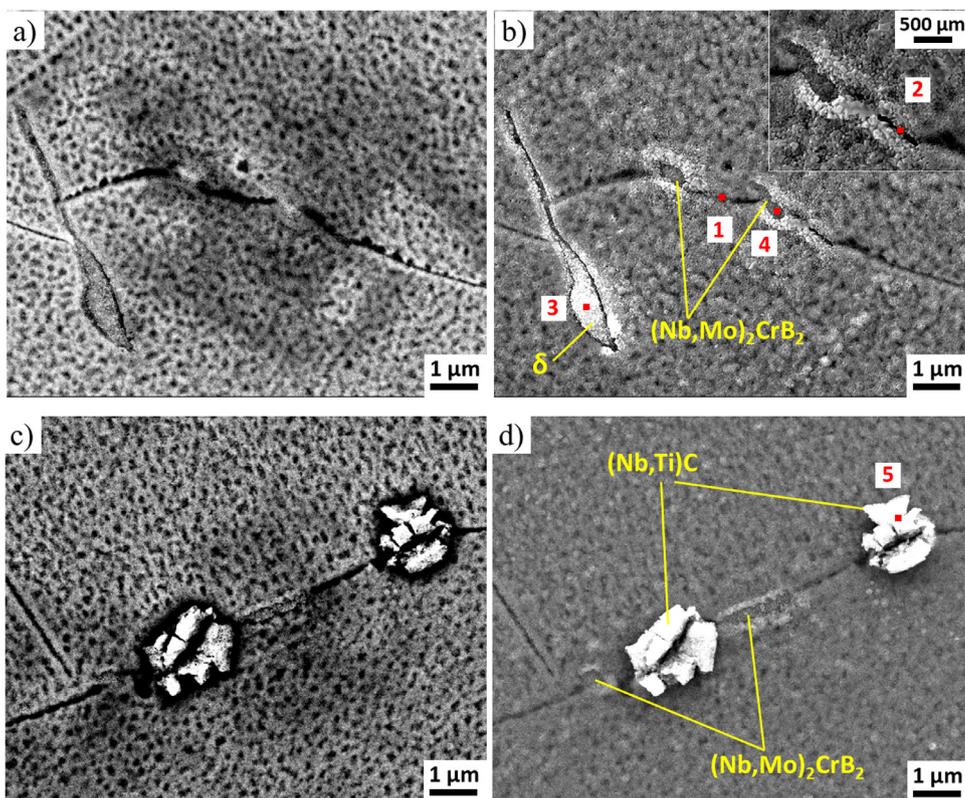


Fig. 6. Intergranular phases involved in the spots. Left column: BSE images. Right column: SE images. a) and b): ST-10 type sample oxidized for 1.5 min at one time. Oxidized δ and $(\text{Nb},\text{Mo})_2\text{CrB}_2$ precipitates are evidenced at the grain boundary but only the $(\text{Nb},\text{Mo})_2\text{CrB}_2$ precipitates are involved in the spot. c) and d): ST-60 type sample oxidized for 1.5 min at one time. Oxidized $(\text{Nb},\text{Ti})\text{C}$ and $(\text{Nb},\text{Mo})_2\text{CrB}_2$ precipitates are evidenced at the grain boundary but only the $(\text{Nb},\text{Mo})_2\text{CrB}_2$ precipitates are involved in the spots. The chemical compositions measured at the points labelled from 1 to 5 are reported in Table 3.

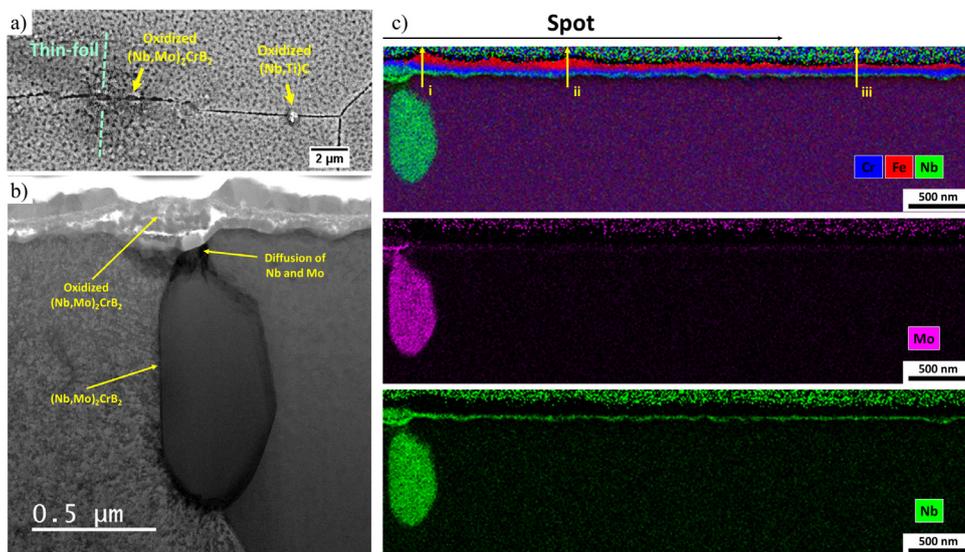


Fig. 7. Cross-sectional view of the oxide film inside a spot. ST-30 type sample oxidized for 0.5 min + 1 min + 1.5 min. a) BSE image. Several oxidized $(\text{Nb},\text{Mo})_2\text{CrB}_2$ borides are observed in a spot. A thin-foil lift-out was performed across one of these oxidized borides following the dotted line. b) Bright field STEM image of the thin-foil positioned in a). A non-oxidized boride is located just below the oxide film. c) TEM-EDX elemental maps acquired at 200 kV. Within the spot, the oxide film exhibits the same 3 oxide layers as those observed outside of the spots (see Fig. 4 and Fig. 5). The chemical compositions quantified along the profile lines i, ii and iii are presented in Fig. 8. The profile lines i and ii cross the oxide film within the spot, while the profile line iii crosses the oxide film outside the spot.

catch some boron segregated inside the grain boundaries (pink arrow in Fig. 11.b). However, in general no significant boron content was measured in the γ matrix before oxidation. The theoretical boron content of the $(\text{Nb},\text{Mo})_2\text{CrB}_2$ borides is 40 at.%. Here, because the volume analyzed by the EPMA technique was larger than the borides, only 30.03 at.% on average was quantified on the borides before oxidation. After oxidation, this boron content was reduced to 4.95 at.%. Such drop in boron content evidenced that boron, like molybdenum, tended to volatilize during the oxidation process. Furthermore, after oxidation much more boron was measured when pointing at the oxidized matrix near grain boundaries (Fig. 12): some significant peaks (i.e. higher than 1000 ppmw) were noticed along the profile lines. In addition, higher boron peaks (blue arrows in Fig. 12) were observed inside the spots

compared to outside the spots. The boron peaks measured after oxidation suggested that during the oxidation process boron atoms diffused towards the sample surface to be incorporated to the oxide scale, as reported in the works of Nowak et al. [10] and Jalowicka et al. [11]. One could assume that the spots showed higher boron peaks because of the redeposition of boron oxide after volatilization from the borides, since borides were very frequent inside the spots. This scenario could account for the vitreous zones at the top of the oxide film. However, this scenario could not explain other specificities of the spots: the increased thickness of the oxide layers (especially of the inner oxide layer) and the different chemical composition of the spinel layer. Thus, if higher boron peaks were measured within the spots it was because these areas were more concentrated in boron before oxidation. Indeed, a higher boron concen

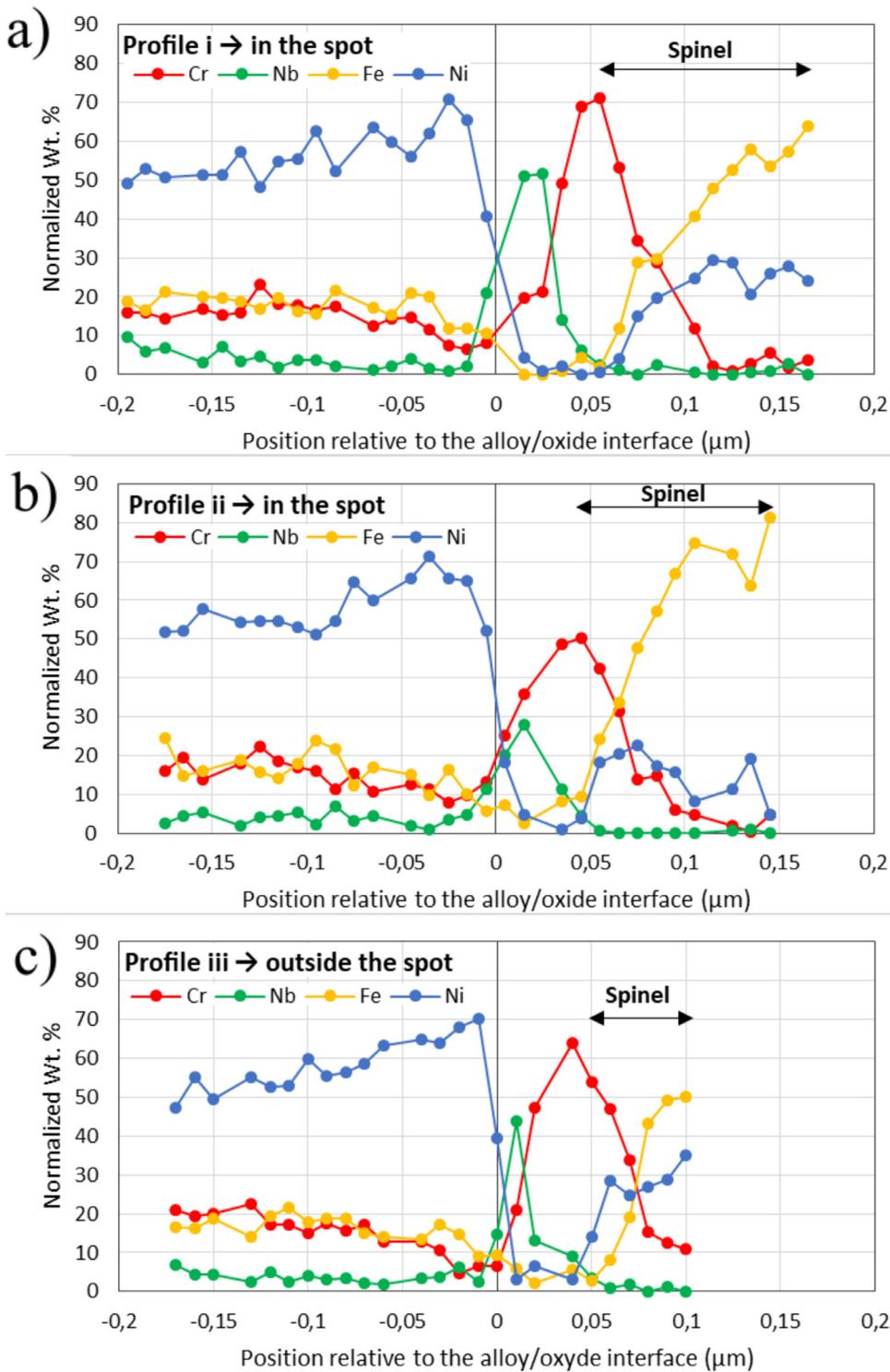


Fig. 8. Chemical compositions quantified along the three profile lines defined in Fig. 7.c. ST-30 type sample oxidized for 0.5 min + 1 min + 1.5 min. TEM-EDX data acquired at 200 kV, normalized wt.%, carbon and boron were omitted from the quantifications. The zero position corresponds to the alloy/oxide interface: negative positions are located in the matrix and positive positions are located in the oxide film. a) Profile line i. b) Profile line ii. c) Profile line iii. The profile lines i and ii cross the oxide film within the spot, the profile line iii crosses the oxide film outside the spot.

tration within the spots could explain the thicker oxide layers and the different chemical composition of the spinel layer since boron is known to increase the oxidation rate by affecting the composition of the oxide scale [8,9]. Before oxidation, the areas with high boron contents could not be detected with the EPMA technique since the boron concentration in these areas was still below the EPMA detection limit: the EPMA detection limit is typically 0.01 wt.% [37] while the nominal boron concentration of the alloy was 0.0038 wt.%. The oxidation process concentrated in the oxide film the boron atoms initially in solution into the matrix, making them more detectable with the EPMA technique.

One can ask about the origin of such high boron concentrations around grain boundaries. The study presented in [14] evidenced that the fraction of $(\text{Nb},\text{Mo})_2\text{CrB}_2$ phase slightly decreased when the material was solution treated at 1050 °C after a subsolvus δ treatment. Then, if the high boron concentrations around grain boundaries resulted from the dissolution of the intergranular $(\text{Nb},\text{Mo})_2\text{CrB}_2$ borides, the size of the spots should correlate with the duration of the solution treatment performed before oxidation. For instance, one could imagine wider spots as the duration of the solution treatment was increased. However, here the spot width was not correlated to the duration of the

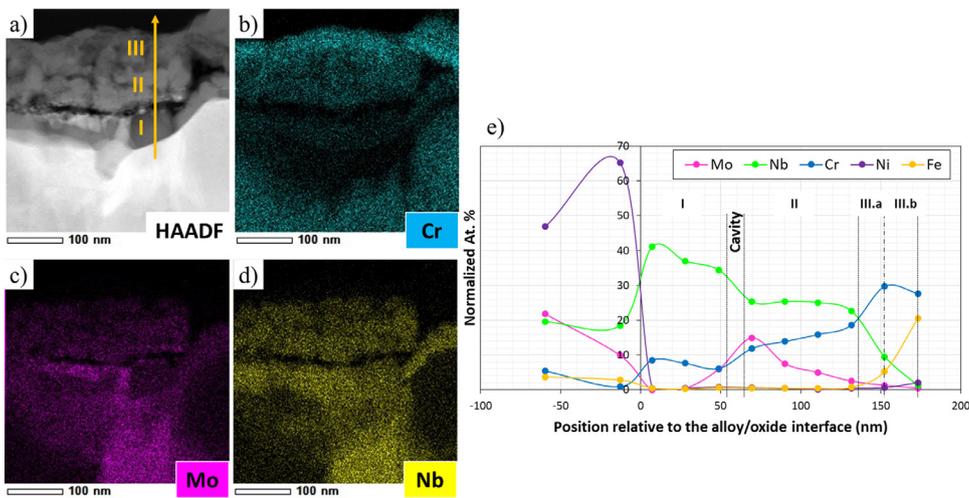


Fig. 9. Oxidation of a $(\text{Nb,Mo})_2\text{CrB}_2$ boride. Oxidized boride of Fig. 7.b. a) HAADF STEM image. b), c) and d): Corresponding STEM-EDX elemental maps acquired at 200 kV. e) Evolution of the Mo, Nb, Cr, Ni and Fe contents along the profile line drawn in a). The zero position corresponds to the alloy/oxide interface: negative positions are located in the alloy and positive positions are located in the oxide film. The region I is the inner oxide layer below the oxidized boride, the regions II, III.a and III.b are different regions of the oxidized boride.

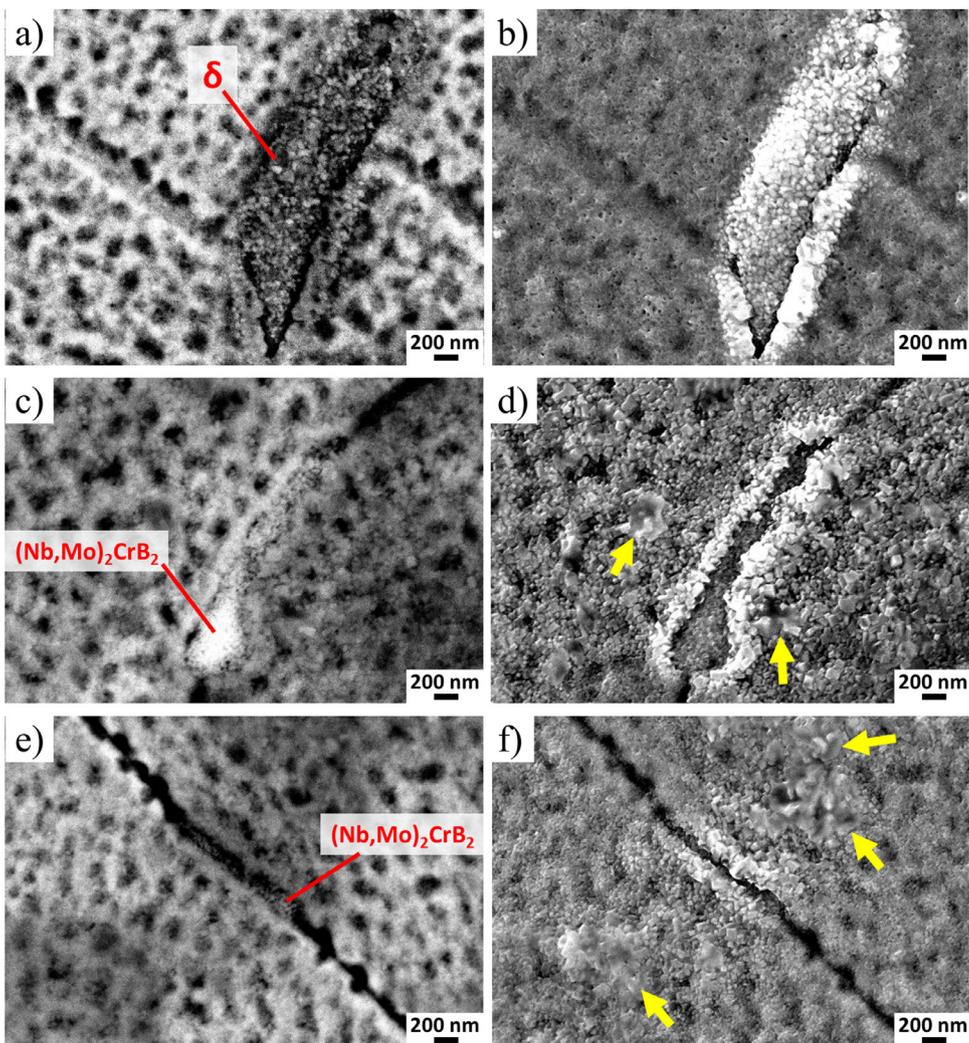


Fig. 10. Upper view of the oxide film outside and inside the spots. From a) to d): ST-10 type sample oxidized for 1.5 min at one time. e) and f): ST-60 type sample oxidized for 1.5 min at one time. Left column: BSE images. The images c) and e) focus on a spot, the image a) has been acquired out of a spot. Right column: SE images. Out of the spots the top of the oxide film appears mat and smooth (b). On the contrary, inside the spots the top of the oxide film appears gleaming and shows protruding crystallites of oxide (d, f). Vitreous zones are also observed inside the spots (yellow arrows in d and f).

solution treatment: the spot widths of the ST 10, ST 30, ST 60 and ST 120 type samples (all oxidized for 1.5 min at one time) were on average 8.1 μm , 5.4 μm , 8.2 μm and 5.3 μm . In addition, several microns did not match with the distance that boron atoms can cover during 120 min of solution treatment at 1050 $^\circ\text{C}$. Indeed, since the diffusion coefficient of boron in nickel based superalloys is approximately 10^{-10} m^2/s at

1050 $^\circ\text{C}$ [15,16,38], the boron atoms should have covered several hundred microns during 120 min of solution treatment. However, several microns is typically the width reported for the non equilibrium segregation of boron around grain boundaries. The non equilibrium segregation of boron around grain boundaries classically occurs when cooling and/or reheating a boron containing alloy [7,16,17,38]. In that case,

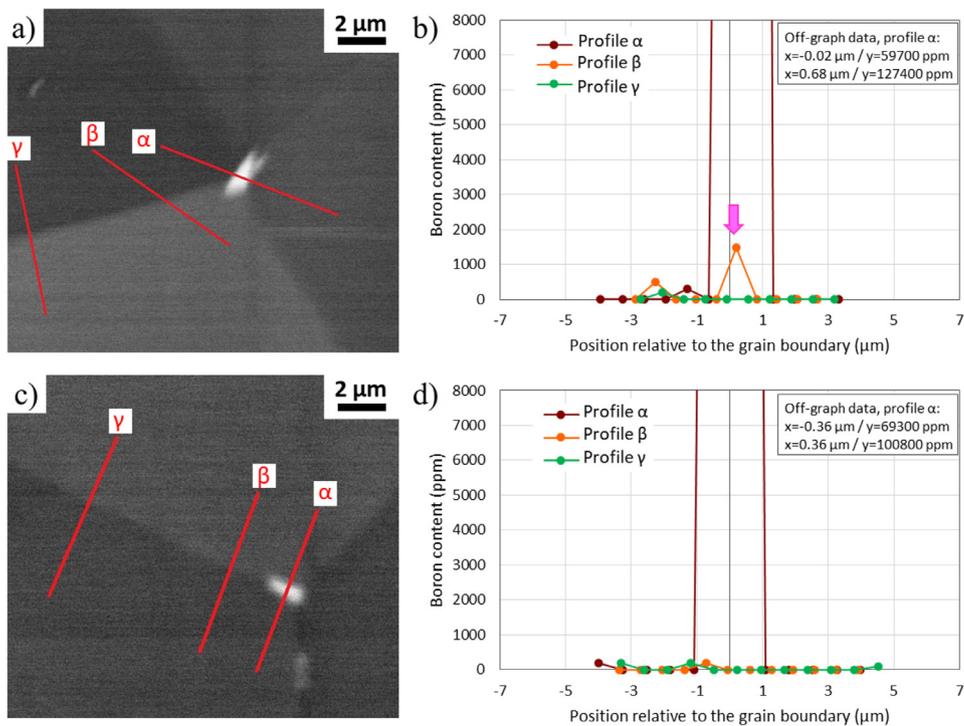


Fig. 11. Boron contents measured with the EPMA technique before oxidation. ST-30 type sample oxidized for 1.5 min at one time. a) and c): BSE images. The red lines figure the profile lines along which EPMA data were acquired: the profile lines α cross an intergranular $(\text{Nb},\text{Mo})_2\text{CrB}_2$ boride, the profile lines β cross a grain boundary segment close to a $(\text{Nb},\text{Mo})_2\text{CrB}_2$ boride and the profile lines γ cross a grain boundary segment far from any $(\text{Nb},\text{Mo})_2\text{CrB}_2$ boride. b) and d): FEG-EPMA results, evolution of the boron content (ppmw) along the profile lines drawn in a) and c). The pink arrow in b) highlights the segregation of boron at grain boundary.

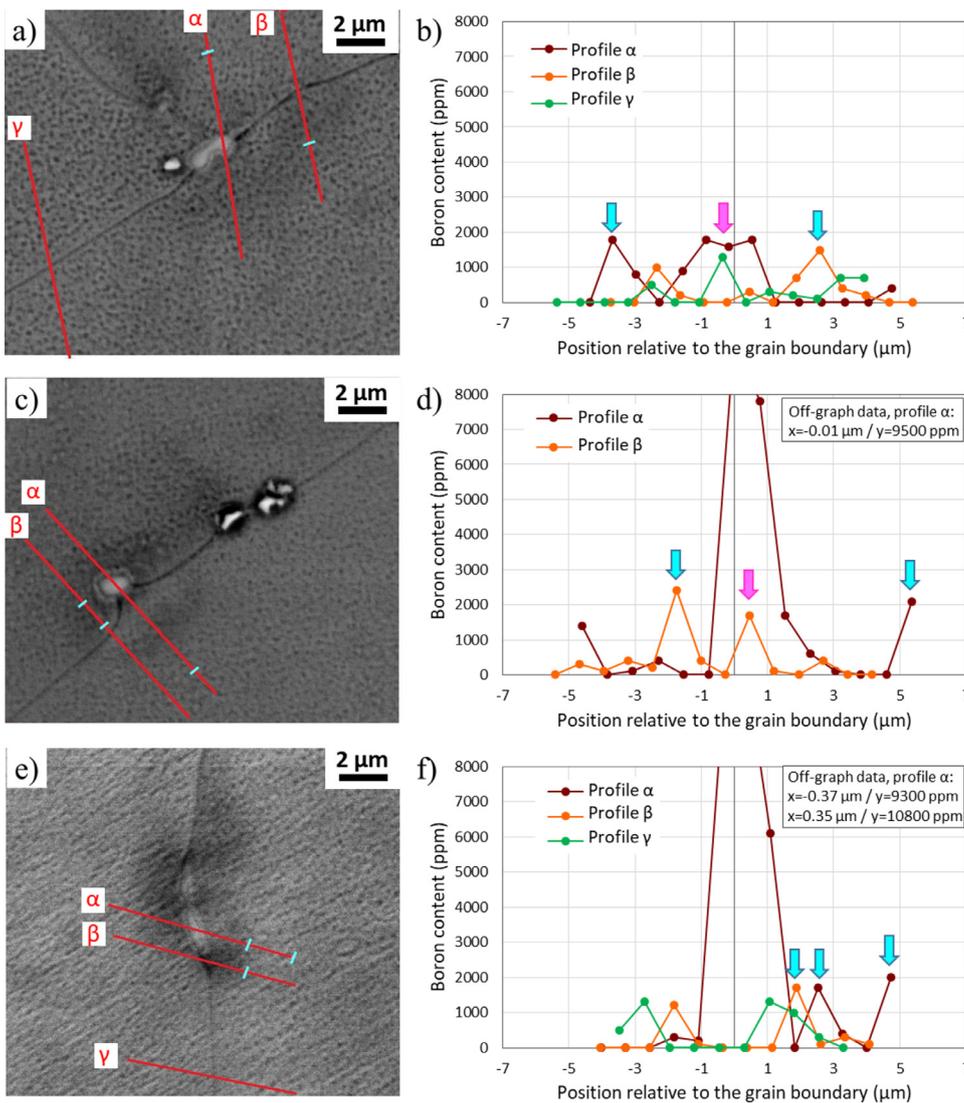


Fig. 12. Boron contents measured with the EPMA technique after flash oxidation. ST-30 type sample oxidized for 1.5 min at one time. a), c) and e): BSE images. The red lines figure the profile lines along which EPMA data were acquired: the profile lines α cross an oxidized $(\text{Nb},\text{Mo})_2\text{CrB}_2$ boride at grain boundary, the profile lines β cross a grain boundary segment in a spot and the profile lines γ cross a grain boundary segment outside the spots. b), d), and e): FEG-EPMA results, evolution of the boron content (ppmw) along the profile lines drawn in a), c) and e). The pink arrows highlight the segregation of boron at grain boundaries. The blue arrows highlight significant boron content enrichments (i.e. > 1000 ppmw), the corresponding points are figured by blue marks along the profile lines in a), c) and e).

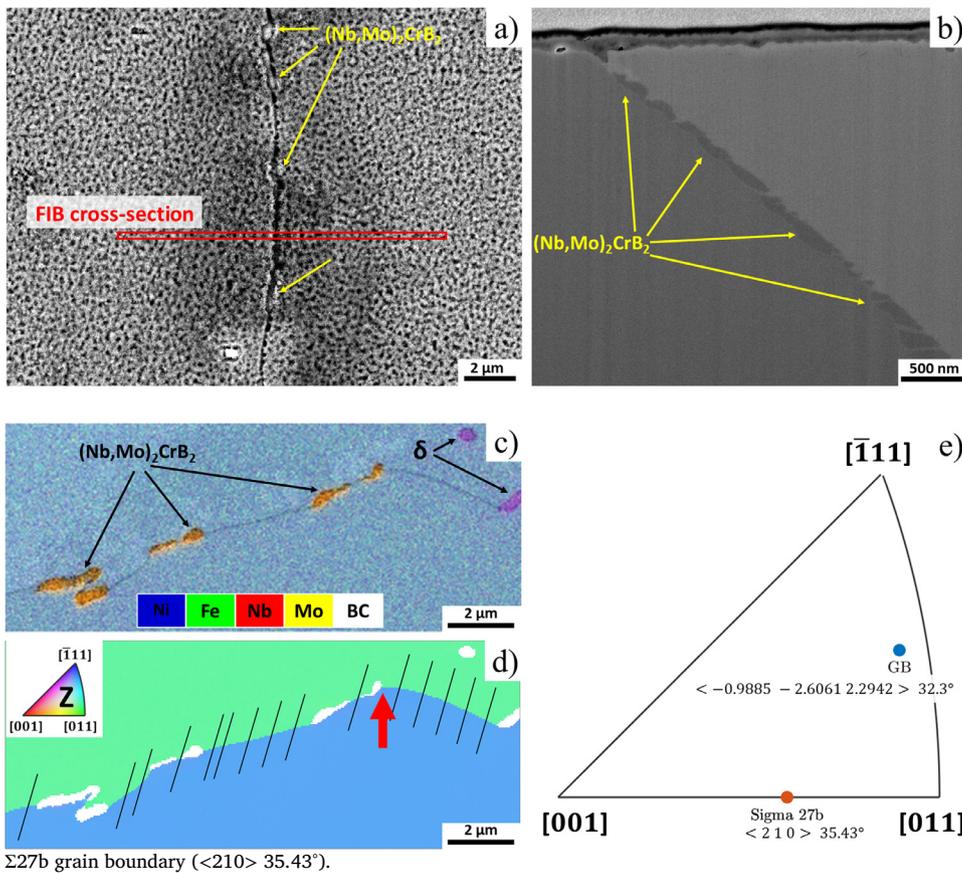


Fig. 13. Examples of grain boundaries with large amounts of $(\text{Nb,Mo})_2\text{CrB}_2$ phase. a) and b): ST-10 type sample oxidized for 1.5 min at one time. c), d) and e): ST-10 type sample before oxidation. a) BSE image which focuses on a spot exhibiting several oxidized $(\text{Nb,Mo})_2\text{CrB}_2$ borides (yellow arrows). A FIB cross-section was performed across the spot, in between two oxidized borides. b) SE image acquired during the FIB cross-section positioned in a). The yellow arrows highlight an almost continuous film of $(\text{Nb,Mo})_2\text{CrB}_2$ phase spreading over 3.5 μm of grain boundary. c) EBSD band contrast map (BC) and EDS map (10 kV) overlapped. Six $(\text{Nb,Mo})_2\text{CrB}_2$ borides are observed over 13 μm of grain boundary. d) EBSD orientation map. The projection of the Z axis (axis perpendicular to the sample surface) within the FCC crystal frame (figured by the standard triangle) sets the color code. The two γ crystals interfacing at the grain boundary are related by a rotation whose angle is 32.3° and whose axis is $\langle -0.9885 -2.6061 2.2942 \rangle$. The black lines along the grain boundary figure the projection of the rotation axis on the acquisition surface. The red arrow points out a change in the grain boundary plane: from this change the grain boundary segment starts being rich in $(\text{Nb,Mo})_2\text{CrB}_2$ phase. e) Inverse pole figure, projection of two rotation axes within the FCC crystal frame (standard triangle): the rotation axis of the grain boundary displayed in d) ($\langle -0.9885 -2.6061 2.2942 \rangle 32.3^\circ$) and that of a

the boron concentrations in the vicinity of the grain boundaries can be several times higher than the equilibrium segregation of boron at the grain boundary interface [16]. Such accumulation of boron solute in the vicinity of the grain boundaries results from the migration of boron vacancy complexes. Indeed, cooling the material generate vacancy gradients from the grain interiors to the grain boundaries, producing a driving force for the migration of vacancies towards the grain boundaries. The vacancies migrate as boron vacancy complexes bringing boron solute to the grain boundaries [16,38]. This way, after water quenching from 1050 °C some samples of superalloy Inconel 718 containing boron, Alam et al. [7] evidenced the segregation of boron around grain boundaries and this segregation measured about 2–3 μm wide. Similarly, after air quenching from 1200 °C some samples of superalloy Inconel 718 containing boron, Chen et al. [16] observed that boron had segregated around grain boundaries and this segregation measured about 5 μm wide. Hence, in the present study, the high boron concentrations evidenced within the spots originated from the non equilibrium segregation of boron which occurred around the grain boundaries during the cooling stage of the solution treatment and/or during the heating stage of the flash oxidation test. Finally, the ST 10, ST 30, ST 60 and ST 120 type samples showed different spot widths probably because of non intentional variations in the experimental procedure. Indeed, according to He [38] and Chen [16], the non equilibrium segregation of boron evolves in only few seconds when cooling or reheating a boron containing alloy. Here, the use of a muffle furnace did not enable to properly control the cooling time after the solution treatment and the reheating time during the flash oxidation tests. Instead, the use of an induction furnace would have probably improved the repeatability of the results.

The discontinuous character of the spots evidenced that before oxidation the non equilibrium segregation of boron was not uniform along the grain boundaries: the non equilibrium segregation was more intense in the areas revealed by the spots and these areas included all the boride

precipitation sites. Several studies in literature have already reported the non uniform segregation of boron at grain boundaries. Chen et al. [16] noticed the influence of the grain boundary misorientation on the non equilibrium segregation of boron in superalloy Inconel 718. From the work of Guo et al. [39] on superalloy Inconel 718, it seems that boron poorly segregates at “Coincidence Site Lattice” boundaries (CSL) with a low reciprocal volume density Σ [40], while non special grain boundaries, which are grain boundaries with a poor atomic fit, seem to favor the segregation of boron. Hence, the segregation of boron at grain boundaries appeared to depend on the grain boundary geometry and thus probably on the grain boundary free energy. Actually, the non uniform segregation of boron within the grain boundary network could have been suspected from the boride distribution. In the present study, like in the studies of Chen [16] and Walsh [41], some grain boundary segments did not exhibit any boride (Fig. 5.a), while some grain boundary segments displayed many borides (Fig. 13.c). Sometimes, an almost continuous film of $(\text{Nb,Mo})_2\text{CrB}_2$ phase was even observed along the grain boundaries (Fig. 13.b). In the present study, the grain boundaries which showed significant amounts of $(\text{Nb,Mo})_2\text{CrB}_2$ phase looked non special grain boundaries. For example, EBSD analyses (Fig. 13.d e) confirmed that the grain boundary displaying six borides in Fig. 13.c was: a high angle grain boundary but neither a CSL boundary with a low Σ value (i.e. $\Sigma \leq 29$, Fig. 13.e) nor a twist boundary (twist grain boundaries can have a low interfacial energy [42]). Furthermore, one could notice that, in Fig. 13.c, the six borides were concentrated on a specific grain boundary plane (the change in the grain boundary plane is highlighted by a red arrow in Fig. 13.d). Yet, it is known that the grain boundary plane has a great influence on the grain boundary free energy [42].

4. Conclusions

The present study investigated the origin of a specific oxidation pattern after the flash oxidation of some superalloy Inconel 718 containing

boron. In optical micrographs and BSE images, this specific oxidation pattern appeared as “spots” located around some grain boundary segments. The main conclusions are the following:

Inside the spots the oxide film exhibited the same 3 oxide layers as those observed out of the spots: likely rutile oxide (Cr,Nb,Ti)O₂, chromia oxide Cr₂O₃ and spinel oxide (Ni,Fe)(Cr,Fe)₂O₄. However, inside the spots the oxide layers were significantly thicker and the outer spinel layer was enriched with iron and depleted of chromium. After flash oxidation, very few δ and secondary (Nb,Ti)C precipitates were observed within the spots. On the contrary, all the (Nb,Mo)₂CrB₂ borides were found involved in a spot, suggesting a connection between the spots and the boride precipitation sites.

Inside the spots, the top of the oxide film was gleaming and exhibited vitreous zones, which strongly suggested the presence of boron oxide at the top of the oxide film.

FEG EPMA analyses evidenced that during the oxidation process the boron atoms which were initially in solid solution in the matrix were incorporated in the oxide scale. Higher boron contents were measured inside the spots: the spots actually reflected areas where boron was highly concentrated before oxidation. Such high boron concentrations near grain boundaries arose from the non equilibrium segregation of boron which classically occurs when cooling and/or reheating a boron containing alloy. The discontinuous character of the spots evidenced that the segregation of boron at grain boundaries was not uniform: boron concentrated at some grain boundary segments with probably a high free energy.

The flash oxidation tests performed in the present study appeared as an original thermal etching technique for revealing the grain boundary segments where boron segregates the most and consequently the boride precipitation sites.

Declaration of Competing Interest

None.

Acknowledgments

The authors thank the STAE foundation (Sciences et Technologies pour l'Aéronautique et l'Espace) for the funding of the present study. They are also grateful to the staff of the UMS Raimond Castaing (Toulouse, France) who provided a precious support for the characterization of the microstructures.

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