USE OF THE EBSD TECHNIQUE TO STUDY THE ROLE OF THE ALLOY-GRAIN-BOUNDARY CHARACTER DURING HIGH-TEMPERATURE OXIDATION OF THE INCONEL 718

Vicente Braz Trindade[1]
Ulrich Krupp[2]
Philip Wagenhuber[3]
Hans-Jürgen Christ[4]

Abstract

In this paper the role of grain-boundary character on the high temperature oxidation behaviour of superalloy 718 is reported focusing on the relationship between the fraction of special grain boundaries, their connectivity and how the oxidation resistance of this alloy can be improved by changing the grain-boundary character by applying a grain-boundary-engineering-type processing. Grain-boundary tailoring was achieved using a grain-boundary-engineering-type processing. A thermomechanical processing cycle corresponds to 20% cold rolling followed by heat treatment at 1050°C in laboratory air and followed by water-quench. Oxidation tests on the Ni-base superalloy IN718 were carried out at temperatures between 850°C and 1000°C using thermogravimetry supported by analytical scanning electron microscopy in combination with EBSD (electron back-scattered diffraction). Evaluation of oxidation kinetics have revealed that special grain boundaries with a high fraction of coincident lattice sites (low Σ values) seem to exhibit a higher resistance to intergranular attack as compared to random high-angle grain boundaries. Hence, grain-boundary engineering might be a promising way to improve high-temperature oxidation resistance.

Keywords: Grain-boundary engineering; Intergranular oxidation; EBSD; Alloy 718.

USO DA TÉCNICA DE EBSD PARA ESTUDAR O PAPEL DO CARÁTER DO CONTORNO DE GRÃO DURANTE OXIDAÇÃO EM ALTAS TEMPERATURAS DA SUPERLIGA INCONEL 718

Resumo

Neste artigo é reportado o papel do caráter do contorno de grão no comportamento da superliga 718 durante oxidação em altas temperaturas, focando na relação entre o percentual de contornos de grão especiais, suas conectividades e como a resistência a oxidação pode ser melhorada através da mudança do caráter do contorno de grão empregando a engenharia do contorno de grão. O ciclo do processamento termomecânico realizado corresponde a 20% de deformação a frio seguido de um tratamento térmico a 1050°C no ambiente de laboratório acompanhado de têmpera. Os testes de Oxidação da superliga 718 foram realizados em temperaturas entre 850°C e 1000°C usando um sistema de termogravimetria e as análises foram realizadas com microscópio eletrônico de varredura em combinação com o sistema de EBSD (electron back-scattered diffraction). Avaliação da cinética de oxidação revelam que contornos de grão especiais com uma elevada fração de sítios de rede coincidentes (baixo valor de Σ) parecem exibir uma elevada resistência ao ataque intergranular comparado com os contornos de grão aleatórios (random) de alto ângulo. Sendo assim, a engenharia do contorno de grão parece ser uma técnica promissora para melhorar a resistência a oxidação em altas temperaturas.

Palavras-chave: Engenharia do contorno de grão; Oxidação intergranular; EBSD; Superliga 718.

[1] *Technical Contribution to the 61st International Congress of the ABM, January 24-27th 2006, Rio de Janeiro – RJ – Brazil.*
[2] *Quality and R&D Manager, Dr.-Ing., Tubos Soldados Atlantico – TSA (Brazil) and Universität*
[3] *Siegen (Germany), vicente.trindade@tsa.ind.br, vicentebraz@yahoo.com.br*
[4] *Senior Engineer, Dr.-Ing., Institut für Werkstofftechnik – Universität Siegen (Germany)*
[5] *Researcher, Dipl.-Ing., Institut für Werkstofftechnik – Universität Siegen (Germany),*
[6] *Professor, Dr.-Ing. habil., Institut für Werkstofftechnik – Universität Siegen (Germany)*

1 INTRODUCTION

The design of alloys for use in corrosive atmospheres at high temperatures is usually done by optimisation of their chemical compositions. In this sense, chromium and aluminium are widely used as elements capable of protecting the alloys against corrosive attack of the parent metal through the formation of a protective external oxide scale, e.g., chromia or alumina. However, internal corrosion can be observed in several alloys even underneath a dense external scale.(1) The ingress of corrosive species, such as oxygen, into the alloy is governed either by dissociation of the superficial oxide at the scale/metal interface and/or penetration along defects of the scale such as cracks and pores.(2) It has been observed that internal oxidation in Ni-base alloys at moderate temperatures (<900^{o}C) occurs preferentially along substrate grain boundaries.(1,3,4)

It is well known that grain boundaries exhibit properties substantially deviating from those of the bulk material, e.g., high diffusivity, depending on its character.(5,6) In a general way, the population of grain boundaries is classified into two categories:(7) (i) random grain boundaries, which are characterized by a high value of Σ, and (ii) special boundaries which are characterized by a low Σ value, Σ being the reciprocal density of coincident lattice sites. Experimental data have confirmed that grain boundaries with $\sum \leq 29$ have special properties,(7-10) i.e., a high fraction of them decreases the susceptibility to intergranular corrosion,(11-13) creep damage(14,15) and dynamic embrittlement.(16) Based on this, these grain boundaries are termed “special boundaries”.(17)

The concept of grain-boundary design was first introduced by Watanabe(10) and used within the studies mentioned above. It is based on a thermomechanical processing technique including several sequences of cold working and annealing, aiming at the increase in the fraction of special grain boundaries and breaking up the connectivity of the random grain boundary network.(18) As a consequence of this, phenomena such as intergranular corrosion can be totally or partially suppressed.(11,13,19)

In this paper the role of grain-boundary character on the high temperature oxidation behaviour of superalloy 718 is reported focusing on the relationship between the fraction of special grain boundaries, their connectivity and how the oxidation resistance of this alloy can be improved by changing the grain boundary character by applying a grain-boundary-engineering-type processing.

2 MATERIAL AND EXPERIMENTAL PROCEDURE

The material used in this study was the superalloy 718 (IN718). Its chemical composition is given in Table 1. The as-received material taken from a forged ring was solution annealed in laboratory air at 1050^{o}C for 1 h followed by water quenching. After that it was aged for 12h at 720^{o}C and for further 12h at 620^{o}C in laboratory air, finally cooled in air to establish the appropriate precipitation of the γ’ (Ni_3Al) phase and the γ’’ phase ($Ni_3(Nb,Al,Ti)$). A 9mm thick plate was used for thermomechanical processing. Therefore, the samples for thermogravimetric testing could be taken from the center of the plate in order to avoid any effect of prior oxidation.

Table 1. Chemical composition (in wt.%) of IN718.

Fe	Cr	Nb	Mo	Ti	Al	Co	Si	Mn	C	B	Ni
18.7	18.2	5.2	3.0	1.0	0.5	0.1	0.4	0.06	0.04	0.004	Bal.

Grain-boundary tailoring was achieved using a grain-boundary-engineering-type processing as described in Krupp et al.[16] and schematically represented in Figure 1. A thermomechanical processing cycle (TMC) corresponds to 20% cold rolling followed by heat treatment at 1050°C in laboratory air and followed by water-quench.

The grain-boundary-character distribution after different thermomechanical processing cycles was measured using electron back-scattered diffraction (EBSD) on a Philips-XL30 scanning electron microscope (SEM). The analysis was carried out using the OIM™ software by TSL (7,20). Specimens for EBSD analysis and oxidation experiments were taken after the first TMC, second TMC and the fourth TMC. The specimens were carefully grounded and mechanically fine-polished using a 0.05µm SiO_2 emulsion on a vibration-polishing machine for a duration of 10h resulting in a smooth and disruption-free surface that is required to get high-quality Kikuchi pattern.

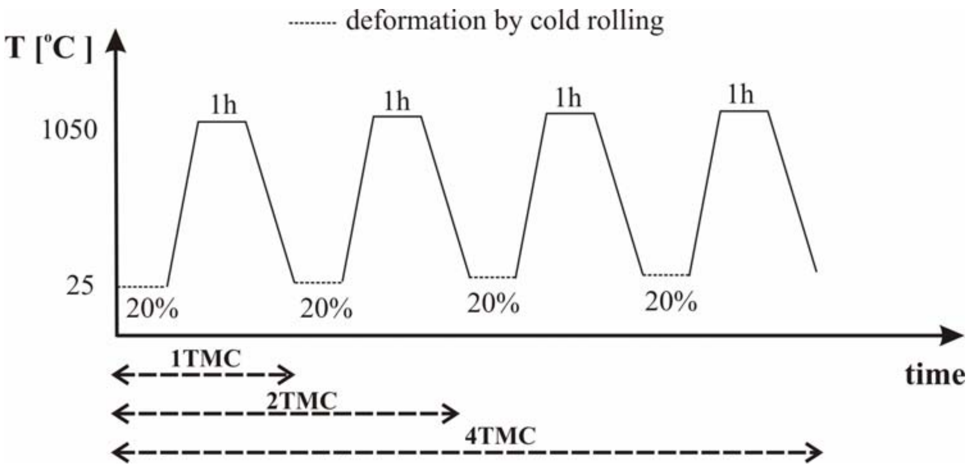
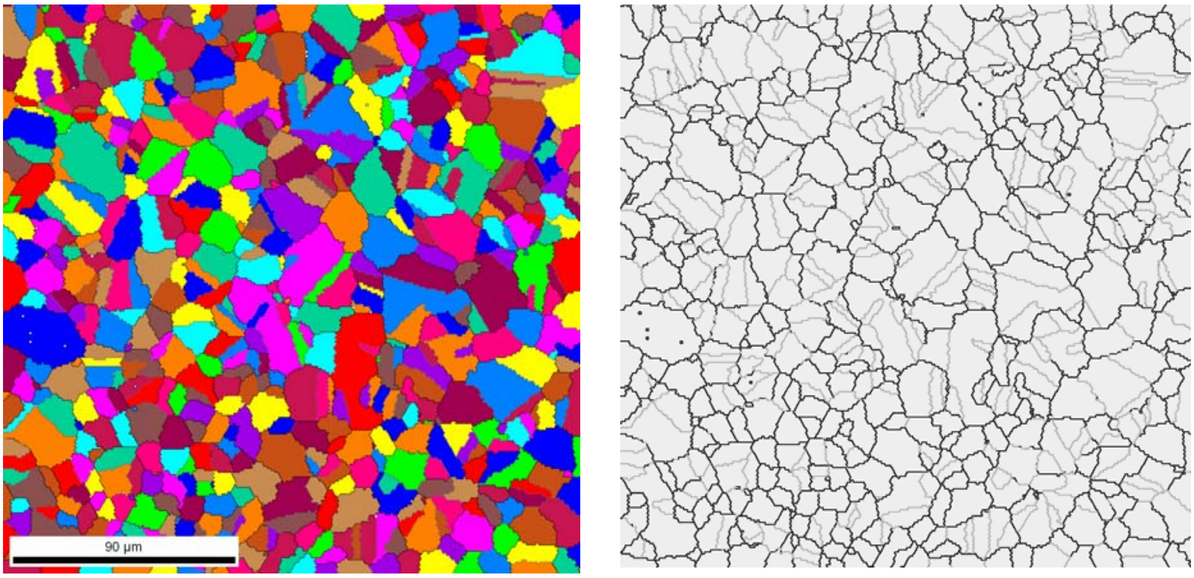


Figure 1. Schematic representation of the thermomechanical processing procedure used in this work.[21]

To quantify the effect of the fraction of special grain boundaries on the oxidation kinetics, specimens with dimensions (10x10x2)mm^3 were ground down to 1200 grit SiC paper, ultrasonically cleaned in ethanol and exposed at 850°C and 1000°C to air for 100h. The mass change during oxidation was measured using a Sartorius microbalance with a resolution of 10^{-5}g. After oxidation, the specimens were embedded in a conductive epoxy resin for SEM and EBSD analysis of the oxidation products.

3 RESULTS AND DISCUSSION

Repeated thermomechanical processing as described above (1-4 TMC) yielded considerable changes in the structure of the grain boundaries (Figure 2). As it can be seen clearly in Table 2 the amount of twin boundaries (coherent Σ3) after 4TMC increases. The mechanism responsible for these changes can be described by the storage of a small amount of energy in the metal during the cold working process through the creation of various lattice defects. After annealing, recovery occurs in the region of the grain boundaries reducing the mismatch between the boundaries and causing the conversion of a part of the high-energy boundaries (random grain boundaries) into low-energy boundaries (special grain boundaries).



(a) (b)

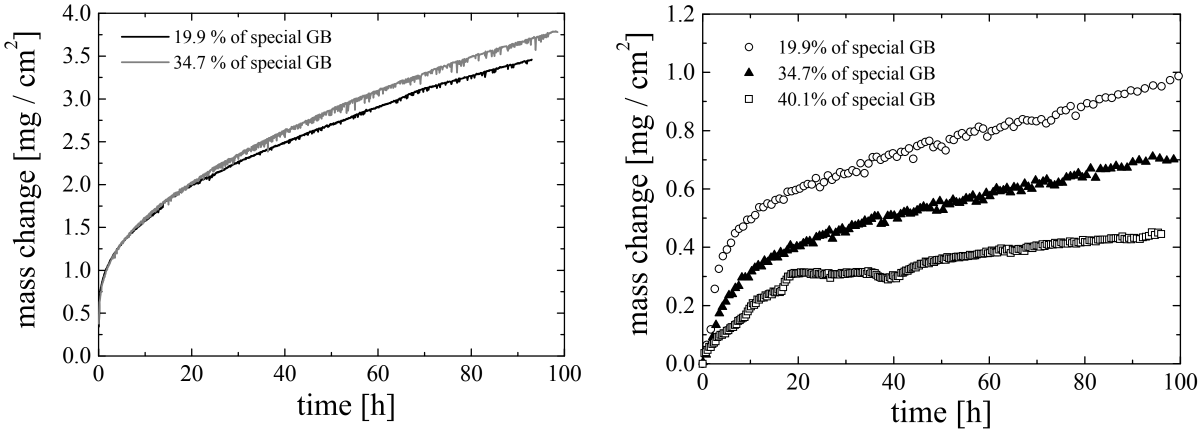
Figure 1. (a) Orientation map and (b) CSL grain boundary distribution (special grain boundaries are marked as gray lines.[21]

Table 2 shows quantitatively the increase in the fraction of special grain boundaries (mainly Σ3 boundaries) after subsequent themomechanical treatment.

Table 2. Fraction (in %) of special boundaries - CSL GBs ($\sum \leq 29$) after different thermomechanical cycles.

Σ value	1TMC	2TMC	4TMC
3	12.9	28.7	35.1
5	0.6	0.7	0.8
7	1.0	0.7	0.5
9	1.2	1.1	1.2
11	0.6	0.6	0.6
13	0.5	0.5	0.4
15	0.5	0.4	0.5
17	0.5	0.2	0.4
19	0.3	0.3	0.4
21	0.5	0.2	0.3
23	0.3	0.1	0.2
25	0.5	0.4	0.4
27	0.3	0.5	0.5
29	0.3	0.4	0.3
fraction of special boundaries	19.9	34.7	41.6

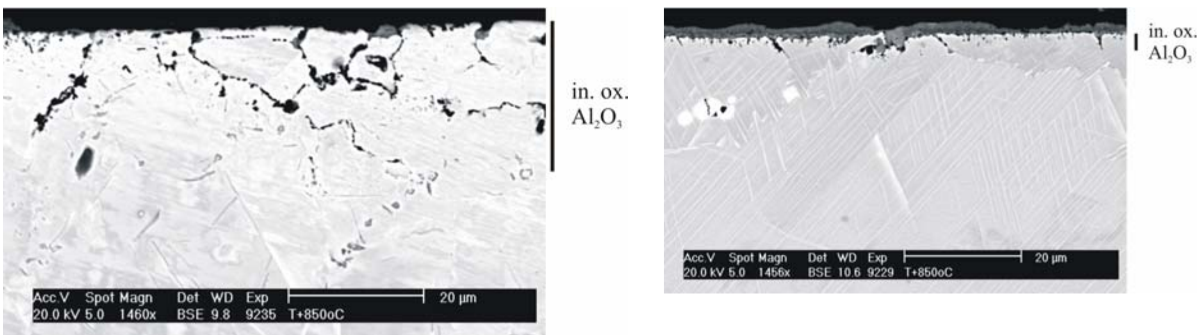
Figure 3a shows the oxidation kinetics at 1000°C for two specimens containing different fractions of special grain boundaries. The oxidation kinetics follows the parabolic rate law similar to that measured by Greene et al.[22] There is only a slight influence of grain-boundary character on the oxidation kinetics of alloy 718 at 1000°C. This is because at very high temperatures the diffusivity along grain boundaries is the same order of magnitude than bulk diffusion[23] and hence, the depth of internal oxidation is independent on the alloy microstructure. However, at lower temperature of 850°C a significant change in the oxidation kinetics was observed for different fractions of special grain boundaries (Figure 3b), which can be attributed to a variation in the internal oxidation attack. It should be mentioned that the specimen containing 40.1% of special grain boundaries has been taken from the material in the as-received condition. For some reason (not investigated in this study, but probably due to the thermomechanical forging process) the fraction of special grain boundaries is higher than in the subsequent TMC.



(a) (b)

Figure 3. Thermogravimetrically measured mass change during exposure of IN718 to laboratory air for different fractions of special grain boundaries: (a) at 1000°C and (b) at 850°C. [21]

As the fraction of special grain boundaries increases, the flux of oxygen into the alloy decreases due to the lower activation energy for diffusion along special grain boundaries. As a consequence, the oxidation rate decreases when the fraction of special grain boundaries increases (see Figure 3b). As shown in Figure 4 the decreasing in the oxidation rate can be attributed to a lower intergranular oxidation depth (intergranular Al_2O_3).

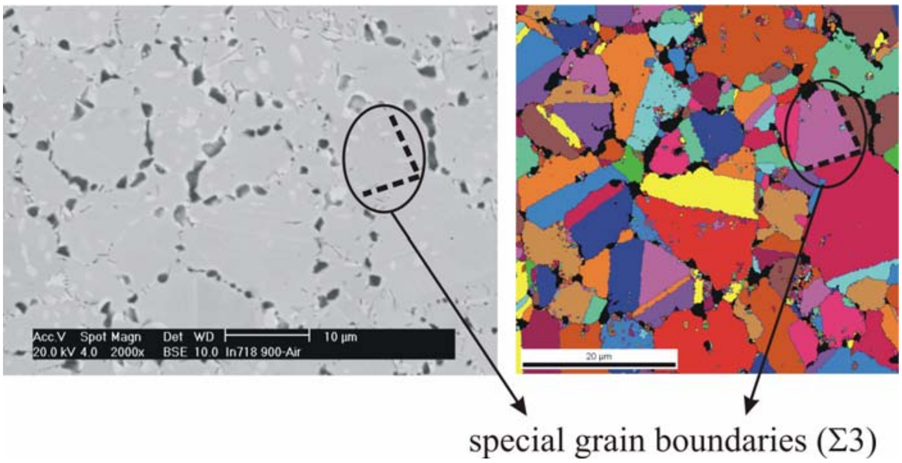


(a) (b)

Figure 4. SEM-cross-section micrographs of the intergranular oxidation zone (in. ox. Al_2O_3) in IN718 oxidised in laboratory air at 850°C: (a) 1TMC* and (b) 4TMC (white areas correspond to δ phase). * Spallation of the outer oxide scale occurred during preparation.

It has to be mentioned that not only the fraction of special grain boundaries, but also the connectivity of special grain boundaries determines the extent of intergranular attack. Thus, a specimen containing a high fraction of special grain boundaries may exhibit a locally deeper intergranular oxidation zone as compared to a specimen with smaller amount of special grain boundaries. This depends on the connectivity of the random grain boundaries as it has been proposed by other authors.[12,13,24] In any case, the absolute number of oxidised grain boundaries is higher for specimens containing less special grain boundaries. This is supported by the kinetic measurements (see Figure 3b) and SEM analysis (see Figure 4a).

Figure 5 shows the preferential formation of internal Al oxide along random grain boundaries, while special grain boundaries remained un-oxidized. This can be interpreted in such a way that the activation energy for oxygen diffusion along special grain boundaries is much higher than that for diffusion along random grain boundaries.[6] This is in agreement with the idea that the diffusivity along special grain boundaries with a high fraction of coincident lattice sites is close to that of bulk diffusion. [6,10]



(a) (b)

Figure 5. Analysis of the surface (the external Cr_2O_3 scale was removed) of an oxidised specimen in laboratory air at 850°C: (a) grain boundary structures and (b) oxide formation along random grain boundaries.[25]

CONCLUSIONS

It has been shown that grain-boundary engineering can be successfully applied to tailor the microstructure of the Ni-base superalloy IN718 in such a way that the susceptibility to intergranular oxidation is reduced. EBSD measurements revealed that special grain boundaries with a high fraction of coincident lattice sites exhibit a high resistance to internal oxidation attack (internal Al_2O_3). Since the reduction of the amount of grain boundaries with high diffusivity (random grain boundaries) gives rise to an additional decrease of intergranular oxidation attack, the overall resistance to high-temperature oxidation can be improved by grain-boundary-engineering-type processing.

Acknowledgements

This research has been supported by Deutsche Forschungsgemeinschaft (DFG KR1999/7-1) and by the Brazilian Research Foundation (CAPES) through a fellowship to one of the authors (V.B. Trindade). This support is gratefully acknowledged.

REFERENCES

1 Douglas, D. L. A critique of internal oxidation in alloys during the post-Wagner era. *Oxid. Met.* **44**, 81-111 (1995).
2 Strawbridge, A., Stott, F. H. and Wood, G. C. The formation and incorporation into the scale of internal oxides developed during the high temperature oxidation of dilute nickel-base alloys. *Corros. Sci.* **35**, 855-862 (1993).
3 Shida, Y., Stott, F. H., Bastow, B. D., Whittle, D. P. and Wood, G. C. Development of preferential intergranular oxides in nickel-aluminum alloys at high temperatures. *Oxid. Met.* **3/4**, 93-113 (1982).
4 Villafane, A. M., Stott, F. H., Nava, J. G. and Wood, G. C. Enhanced oxygen diffusion along internal oxide-metal matrix interfaces in Ni-Al alloys during internal oxidation. *Oxid. Met.* **57**, 267-279 (2002).
5 Palumbo, G. and Aust, K. T. Solute effects in grain boundary engineering. *Canad. Metall. Q.* 34, 165-173 (1995).
6 Farkas, D. Atomistic theory and computer simulation of grain boundary structure and diffusion. *J. Phys. Condens. Matter* **12**, 497-516 (2000).
7 Randle, V. Microstructure determination and its applications. The Institute of Materials, London (1992).
8 Garbacz, A., Ralph, B. and Kurzydlpwski, K. J. On the possible correlation between grain size distribution and distribution of CSL boundaries in polycrystals. *Acta Met. et Mat.* **43**, 1541-1547 (1995).
9 Davé, V. R., Cola, M. J., Kumar, M., Schwartz, A. J. and Hussen, G. N. A. Grain boundary character in alloy 690 and ductility-dip cracking susceptibility. *Welding Journal*,1-5 (2004).
10 Watanabe, T. Approach to grain boundary design for strong and ductile polycrystals. *Res Mech.* 11, 47-84 (1984).
11 Lin, P., Palumbo, G., Erb, U. and Aust, K. T. Influence of grain boundary character distribution on sensitisation and intergranular corrosion of alloy 600. *Scripta Met. et Mater.* 33, 1387-1392 (1995).
12 Yamaura, Y., Igarashi, Y., Tsurekawa, S. and Watanabe, T. Structure-dependent intergranular oxidation in Ni-Fe polycrystalline alloy. *Acta Mater.* **47**, 1163-1174 (1999).
13 Lehockey, E. M., Palumbo, G., Lin, P. and Brennenstuhl, A. M. On the relationship between grain boundary character distribution and intergranular corrosion. Scripta Mater. 36, 1211-1218 (1997).
14 Was, G.S., Thaveeprungsripon, D. C. and Crawford, D. C. Grain boundary misorientation effects on creep and cracking in Ni-based alloys. *JOM* **2**, 44-49 (1998).
15 Lehockey, E. M. and Palumbo, G. On the creep behaviour of grain boundary engineered nickel. *Mater. Sci. Eng. A* **237**, 168-172 (1997).
16 Krupp, U., Kane, W. M., Liu, X., Dueber, O., Laird, C. and McMahon, C. J. The effect of grain-boundary-engineering-type processing on oxygen-induced cracking of IN718. *Mater. Sci. Eng. A*, **349**, 213-217 (2002).
17 Palumbo, G., Lehockey, E. M. and Lin, P. Applications for grain boundary engineered materials. *JOM* **2**, 40-43 (1998).
18 Kumar, M., King, W. E. and Schwartz, A. J. Modifications to the microstructural topology in F.C.C materials through thermomechanical processing. *Acta Mater.* **48**, 2081-2091 (2000).
19 Gertsman, V. Y., Janecek, M. and Tangri, K. Grain boundary ensembles in polycrystals. *Acta Mater.* 44, 2869-2882 (1996).

20 Adams, B. L. Orientation imaging microscopy: Emerging and future applications. *Ultramicroscopy* **67**, 11-17 (1997).
21 TRINDADE, Vicente B.; WAGENHUBER, Phiolip Georg; KRUPP, Ulrich; CHRIST, Hans Jürgen Studying the role of the alloy-grain-boundary character during oxidation of Ni-base alloys by means of the EBSD technique. In: Microscopy of Oxidation, 2005, Birminghan. Microscopy of Oxidation 5. 2005. p.115-125.
22 Greene, G. A. and Finfrock, C. C. Oxidation of Inconel 718 in air at high temperatures. *Oxid. Met.* **55**, 505-521 (2001).
23 Philibert, J. Grain boundary diffusion and oxidation processes. *Solid State Ionics* **117**, 7-11 (1999).
24 Yamaura, S., Tsurekawa, S. and Watanabe, T. The control of oxidation-induced intergranular embrittlement by grain boundary engineering in rapidly solidified Ni-Fe alloys ribbons. *Mater. Trans.* **44**, 1494-1502 (2003).
25 Yang, S., Krupp, U., Christ, H.-J. and Trindade, V. B. The relationship between grain boundary character and the intergranular oxide distribution in IN718 superalloy. *Adv. Eng. Mater.*, **7**, 723-726 (2005).