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HIGH TEMPERATURE INTERGRANULAR OXIDATION OF ALLOY 718

V. Garat[1], J. Deleume[1], J-M. Cloué[1], E. Andrieu[2]

[1]Framatome ANP Fuel Division ; 10, rue J. Récamier ; 69456 Lyon Cedex, France
[2]Centre Inter-Universitaire de Recherche et d'Ingénierie des Matériaux (CIRIMAT) ;
UMR CNRS/INPT/UPS ; 118, Route de Narbonne, 31077 Toulouse Cedex 04, France

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Abstract

Alloy 718 samples were oxidized in air under experimental conditions close to those experienced during high-temperature heat treatments (shaping: about 1000°C) or in service (turbomachine disks: 650°C). The main objective of the study was to evaluate the impact of these treatments on oxygen penetration into the grain boundaries and, hence, to assess the harmfulness of these penetrations in terms of defect initiation and propagation. The method relies mainly on the SIMS-based imaging technique. This technique, which supplements those applied in previous studies, uses a series of basic maps to locate within the volume the oxygen in free or combined state, in relation with the microstructural features (grain boundaries, grains, delta phase, etc). The results point out to intergranular oxidation for both exposure conditions without clearly demonstrating the existence of atomic oxygen penetrations ahead of the intergranular oxidation front. The affected depths seem sufficient both to form preferential initiation sites (oxidation at 1000°C) and to assist intergranular propagation of defects and/or cracks (oxidation at 650°C).

Introduction

The family of nickel based superalloys has been widely used for decades in many industries such as aeronautical, oil, marine, nuclear. Among them, alloy 718 has been used since the 1960s in turbine components and more recently for the structural applications in primary water coolant circuit of pressurized water reactor. Alloy 718 is, as many other nickel based alloys such as alloy 600 or X750 are, sensitive to an oxidation assisted crack growth mechanism. Indeed, many studies have emphasized the detrimental effect of oxygen and more generally of environment on the mechanical behavior of alloy 718 at high temperatures [1-9]. The present paper is aimed at studying the effect of two oxidation conditions close to those encountered industrially:

- 1000°C in air: similar to hot rolling conditions. In spite of surface treatments (e.g. sand blasting, machining), defects can be formed and remain present throughout the industrial working process [10].
- 650°C in air: similar to "in service" conditions of turbomachine disks. Under such conditions, the material is known to be sensitive to oxidation assisted crack propagation [3-13].

The core of the present study is to assess the harmfulness of intergranular oxides penetrations (IOP) on the mechanical properties of alloy 718.

Materials and Experimental Procedures

The material used in this study was obtained through a double melting process: vacuum induction melting plus vacuum arc remelting (4 mm thick plate). The nominal composition of the alloy is given in Table I.

Table I : Chemical composition of alloy 718 (weight %)

Ni	Fe	Cr	Mo	Al	Ti	Nb	Ta	C
50-55	Bal.	17-20	3-3.5	0.2-0.8	0.7-1.2	4.7-5.5	0.1	<0.08

The cast ingot was hot and cold rolled down to the thickness of 4 – 5 mm, followed by a solution annealing heat treatment at 1000°C for one hour ended by air quenching. 1 mm thick tensile specimens were machined by milling from the plate and could then be thinned to the thickness of 0.3 mm along the gage length. This thinning process aims at increasing the damaging effects of environment through a reduction of the ratio surface/volume. Specimens were then heat treated under vacuum following the conventional aeronautical route: hold 720°C-8h, cooling 50°C/h down to 620°C, hold 620°C-8h and final air cooling to room temperature. After the heat treatment, their surfaces were polished using SiC paper and diamond paste to the grade 1 µm in order to remove the heat affected zone and/or the possible oxide formed during treatment. The microstructure of studied product presents a fine and homogeneous precipitation of γ' and γ'' phases. As the heat treatment was optimized on the basis of a low δ phase density criteria, a very few δ phase precipitates (platelets-nodules) was observed. Primary carbides Ti (C,N) and NbC are observed too. Grain size and room temperature mechanical properties of studied tensile specimens are given in Table II.

Table II: Grain size (ASTM grain size number) and mechanical properties (Yield Strength, Ultimate Tensile Strength and Elongation to rupture) of studied specimens at room temperature.

Specimens	Grain size	YS (MPa)	UTS (MPa)	E (%)
1 mm thick	8 – 9	1479	1559	14.1
0.3 mm thick	8 - 9	1218	1420	20.4

Oxide scales, but also underlying alloy, were characterized using different techniques, including SEM (LEO 435VP) and FEG-SEM (LEO 1530) observations. Local determinations of chemical composition were performed using Secondary Ions Mass Spectrometry (SIMS, CAMECA IMS 4F/6F). Resistive Anode Encoder (RAE) mode was selected on the SIMS with an analyzed zone diameter of 30 µm whereas the total area of the abrasion zone was 150 x 150 µm². The RAE mode enables to collect 2D-basic maps of oxygen and the main metals elements constitutive of the alloy (Ni, Fe, Cr, Nb, Al, Ti) throughout the abrasion of the specimen. The calibration of abrasion rate for the specific material and operating conditions has previously been performed [10], by measuring the depth of different cavities using optical interferometry. Consequently, concentration data of the basic maps can be both plotted versus time and/or depth. However, SIMS analyses only provide semi-quantitative information and need to be completed with quantitative data obtained through Glow Discharge Mass Spectrometry (GDMS).
Moreover, in order to avoid the influence of roughness of the oxide scale on the definition of the location of the oxide-alloy interface and to keep the highest sensitivity for crucial elements, namely oxygen, SIMS analysis were performed by starting abrasion from the underlying alloy to the oxide scale. For this purpose, specific specimens were prepared by mechanical polishing. The following procedure (Figure 1) was applied [13, 14]: the coupon was cut to fit SIMS specimen size. After that, its oxidized face was glued on a cylindrical rod (diameter: 30 mm, height: 20 mm) made of copper. The coupon was then mechanically polished on the alloy side down to a thickness of less than 10 µm. A final polishing was done using a colloidal silica suspension (OP-S Suspension ™ Struers).

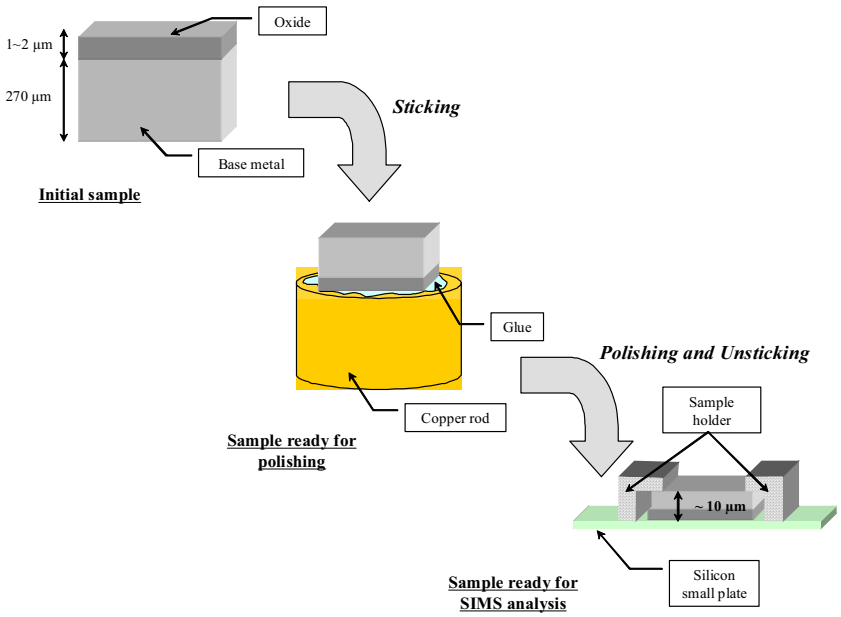


Figure 1: Preparation steps of a sample for SIMS analysis

Experimental Results

Effects of pre-oxidation treatment at 1000°C in air

According to the results of previous studies [7-13], a pre-oxidation treatment at 1000°C in air leads to the formation of IOP under a 1 or 2 µm thick oxide layer. FEG-SEM and SIMS analyses conclusively highlight that phenomenon (Figures 2, 3 and 4.a). Those IOP are homogeneously distributed in the alloy and are deep enough to be considered as crack initiation sites. Indeed, according to EDX analysis (Figure 2) and SIMS RAE maps (Figure 4.a), IOP are mainly constituted by alumina plus other metal oxides but no free oxygen could be detected. The affected depths range from 10 to 15 µm and chromium depletion is observed under the oxide-alloy interface (Figures 2, 3 and 4).
Consequently, the formation of both oxide scale and metal oxides in grain boundaries results in a local depletion of alloying elements in the base metal due to the selective oxidation process (Cr, Al, Ti, Nb). This gradient in the chemical composition of the alloy is clearly shown by 3D reprocessed RAE maps (Figure 4.a). Because of the semi-quantitative aspect of SIMS data, GDMS analysis has been run too in order to collect quantitative data (Figure 4.b). The same kind of results is observed for both tested specimens. SIMS analysis of IOP also proves that the arrangement of the different oxides is in great adequacy with thermodynamics data. Indeed, the deeper under the metal-oxide interface the considered oxide is, the easier to form it is, if considering Ellingham's diagram.

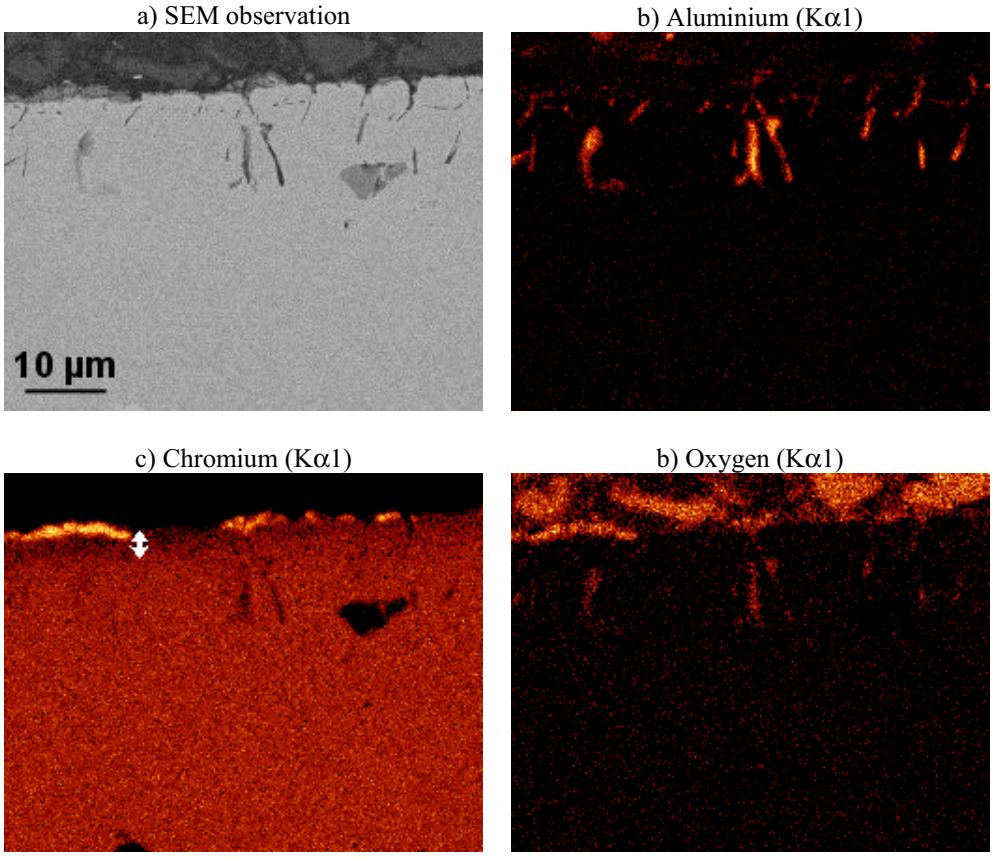
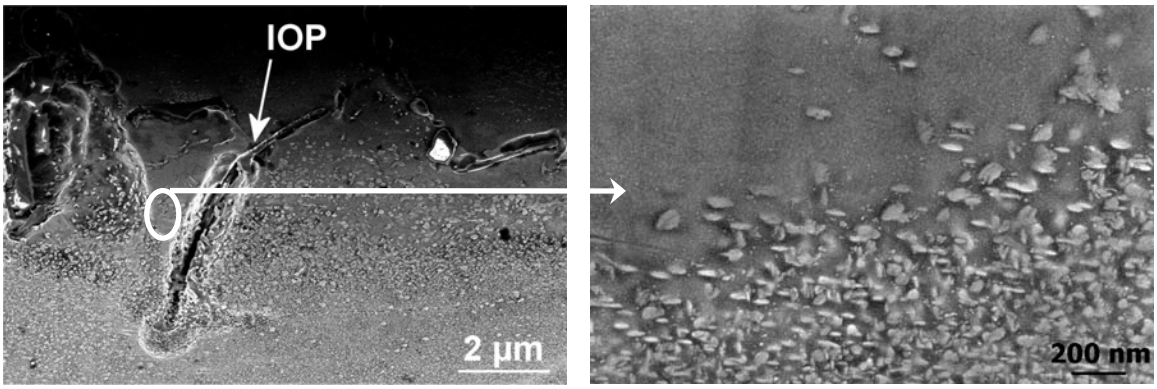


Figure 2: XPS characterization of IOP on cross sectional specimen [13]
(1 mm thick specimen – 1 hour at 1000°C in air)
The double arrow on figure 2.c shows the observed chromium depletion



General view on a cross sectional specimen

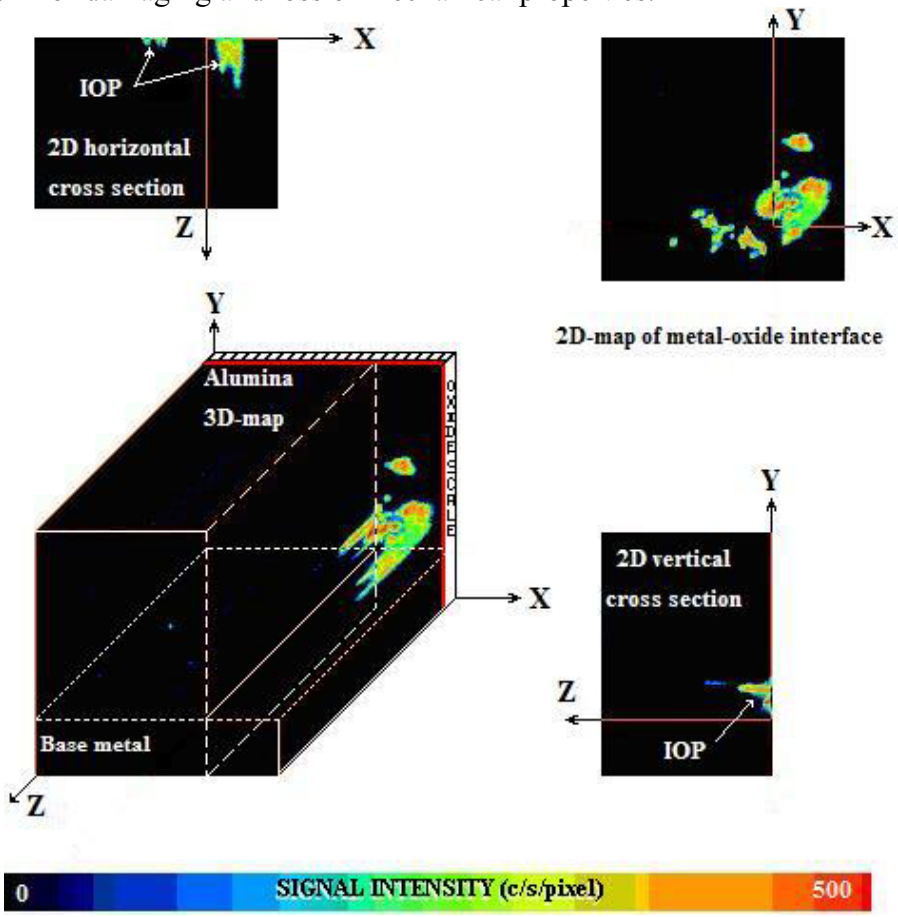
Zoom on a γ' and γ'' depleted area
close to the oxidized surface

Figure 3: Hardening precipitates depletion near IOP
FEG-SEM observations after electrochemical etching (HCl, 2.5 V, 10 s, room temperature)

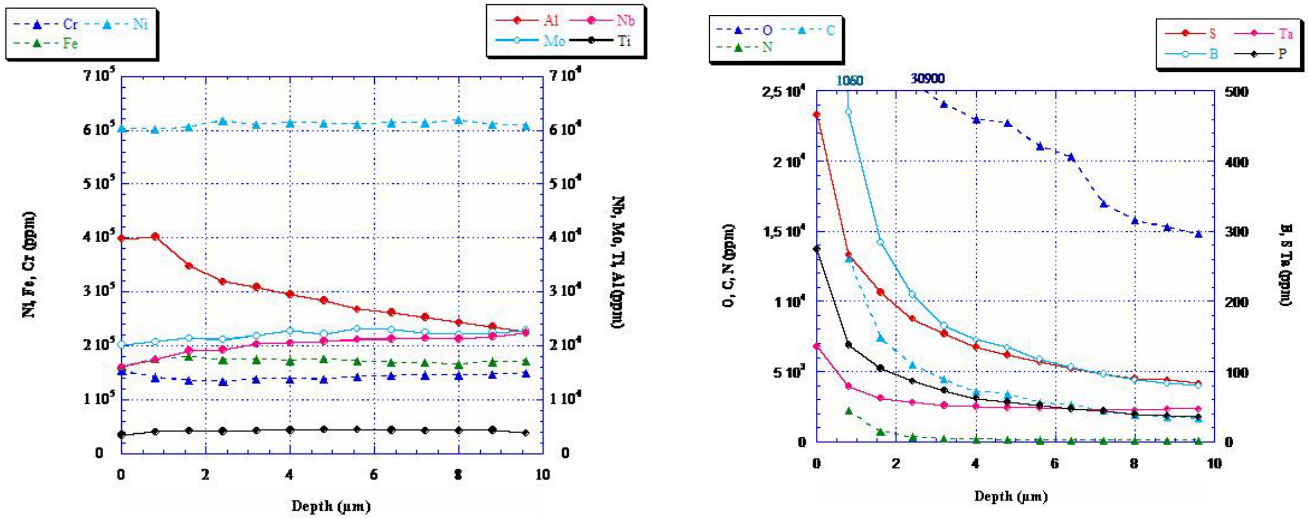
Effect of oxidation in service conditions

To go further in the evaluation of the harmfulness of high temperature oxidation of alloy 718, SIMS analysis were performed on specimens after oxidation at 650°C in air for different times. Analytical data (Figure 5) proves that there's no difference with what is observed at 1000°C: the different oxides still have the same arrangement, in very good adequacy with Ellingham's

predictions; alumina forms at the intergranular oxidation front (affected depth ~ 1 µm) and no measurable dissolved oxygen is found in the alloy ahead of this front. Considering those results, a kinetic study of the phenomena has been performed in order to evaluate critical time of exposure in term of damaging and loss of mechanical properties.



a) 3D reprocessed RAE maps for alumina – Evidence of the formation of IOP



b) GDMS profiles (Analyzed area ≈ 1 cm²) [10]

Figure 4: Analytical evidence of the formation of IOP on tested specimens.

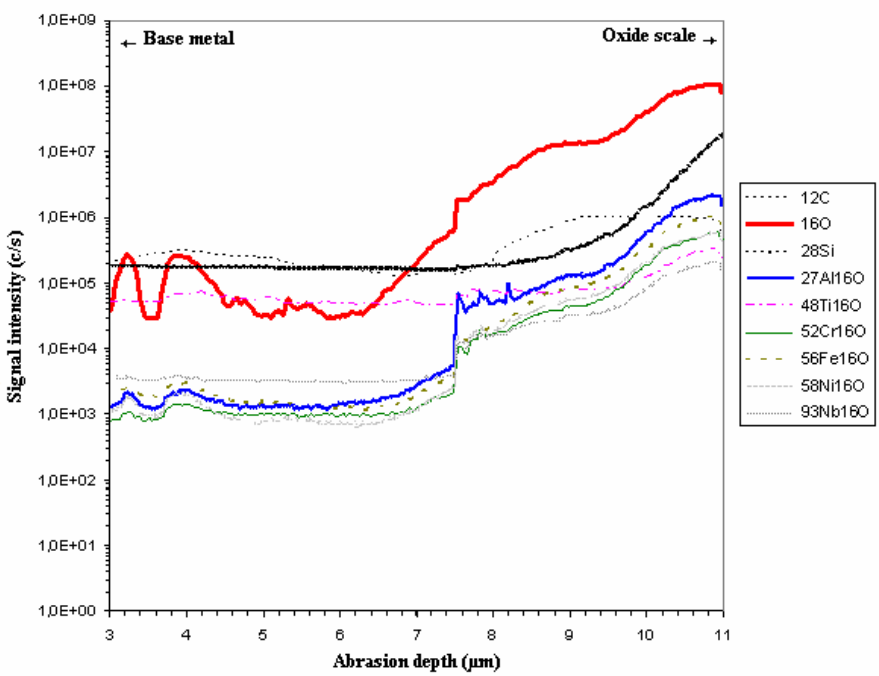


Figure 5: SIMS profiles for a specimen oxidized at 650°C for 15 minutes under air conditions

Kinetic study of the effects of high temperature oxidation on alloy 718 behavior

Since analytical data highlight a depletion in alloying elements which are constitutive of hardening precipitates γ' and γ'', it is expected that mechanical behavior of alloy 718 must be modified, at least at a local scale, by high temperature oxidation process. In order to assess the harmfulness of IOP, tensile tests were performed under imposed strain rate controlled mode ($d\varepsilon/dt = 10^{-3}\ s^{-1}$) in air at room temperature after different pre-oxidation times at 1000°C.

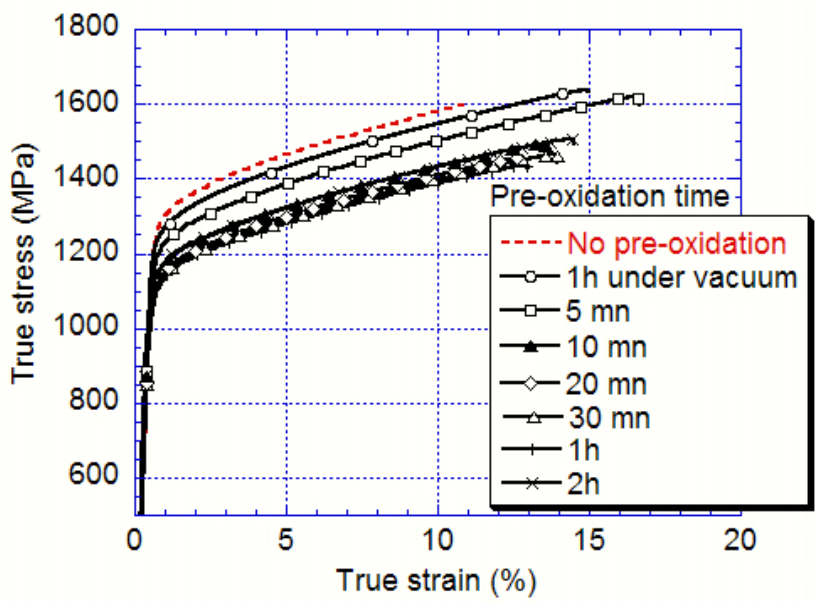


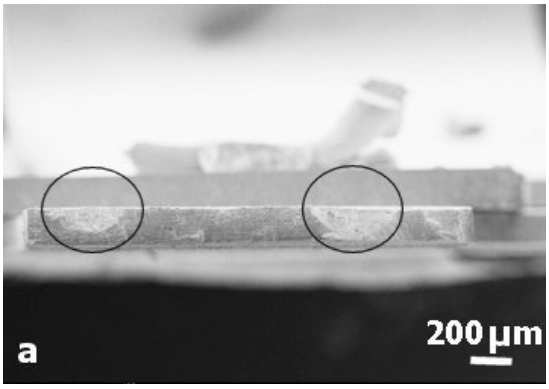
Figure 6: Tensile tests performed at room temperature on 0.3 mm thick specimens (Pre-oxidation at 1000°C in air) [13]

The tensile curves are presented in Figure 6 [13] and focus on three main points:

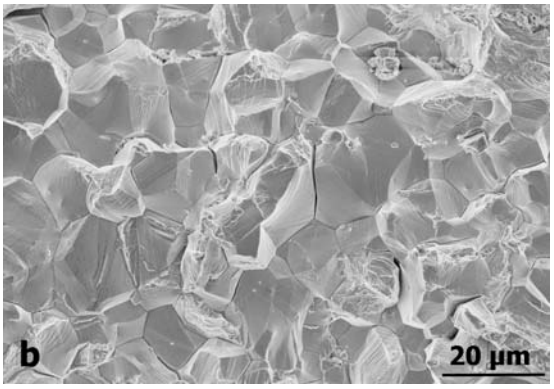
- A pre-oxidation treatment at 1000°C for 1 hour under vacuum results in a loss in term of mechanical properties of alloy 718 at room temperature (- 40 MPa compared to the yield strength of the non pre-oxidized specimen).

- The main part of the damage occurs after 10 minutes of exposition at 1000°C (-100 MPa compared to the yield strength of the non pre-oxidized specimen).
- Consequences of oxidation on the mechanical behavior of alloy 718 are observed at the very beginning of the tensile test and generate a global shift of the tensile curve. It is thus relevant to suppose that there's no localization of strain during the test.

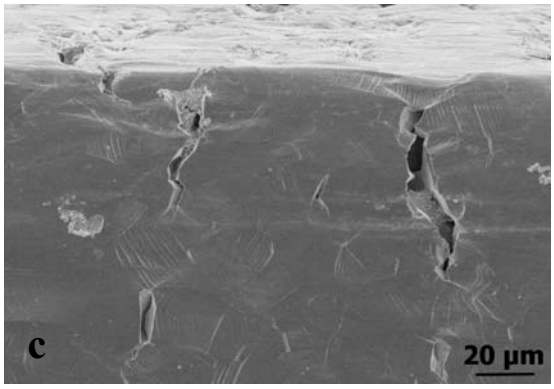
To go further in the evaluation of the harmfulness of intergranular oxidation of alloy 718, tensile tests were also performed at 650°C in air, experimental conditions close to those encountered in service by turbomachines disks. Testing conditions were strictly the same as those performed at room temperature. All tested tensile specimens, whatever their thickness is, reveal a fracture mode which is mainly transgranular ductile but locally intergranular fragile as shown on Figure 7. Such observations have seldom been made on massive forged products, except for particular environmental conditions [15]. All specimens reveal not only several intergranular fragile areas on their fracture surfaces but also intergranular crack initiation sites which can range a depth of more than 60 µm.



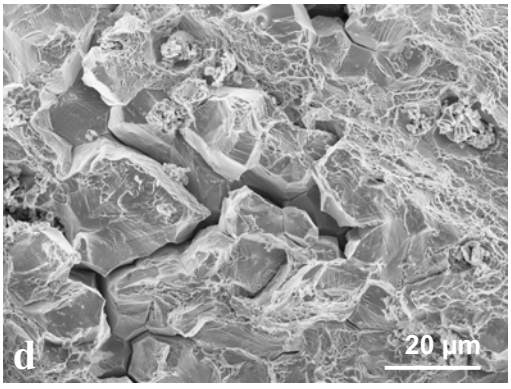
a) General view of the fracture surface of a 0.3 mm thick specimen



b) Zoom on the right circled area on a)



c) Intergranular initiation crack sites on a 0.3 mm thick tested specimen



d) Fracture surface of a 1 mm thick specimen

Figure 7: SEM observation of fracture surface of 0.3 mm and 1 mm thick specimens tested at 650°C in air with an applied strain rate of 10^{-3} s^{-1}.

To assess whether intergranular oxidation is responsible for the loss in mechanical properties observed after high temperature air exposures, two complementary tensile tests were carried out on 1 mm thick specimens, one of them performed under inert atmosphere (ArH_2 with 5% of H_2) and the other one under air at a temperature of 650°C in the same conditions than former. The tensile curves are shown on Figure 8. For both tested environmental conditions, specimens exhibit the same mechanical behavior except the elongation to rupture. In addition, fracture surfaces of specimen tested under inert atmosphere are completely transgranular ductile whereas

oxidized specimen still exhibits intergranular fragile areas. Thus, it is conclusively shown that oxidizing environment help crack propagation owing to what can be presented as an internal oxidation process.

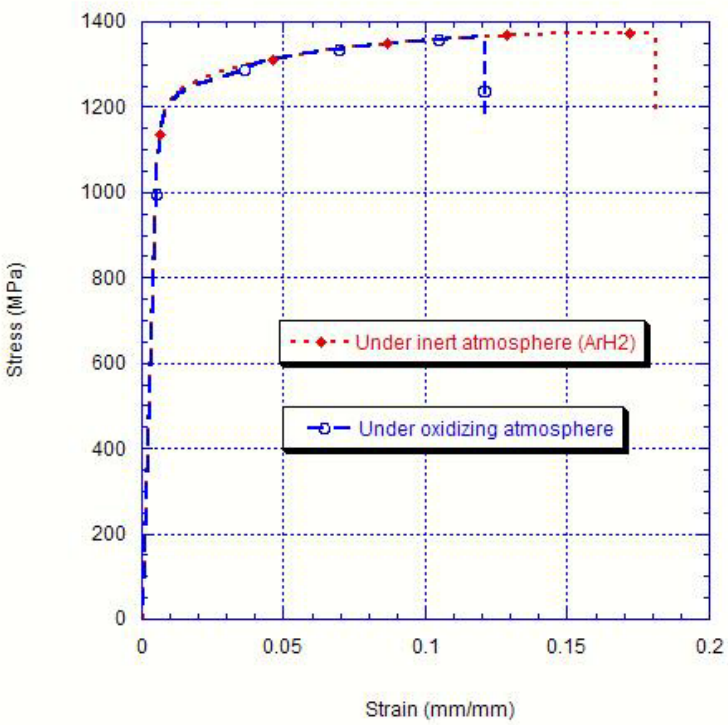


Figure 8: Tensile tests performed at 650°C on 1 mm thick specimens under inert/oxidizing conditions

Finally, in order to complete the study and evaluate the cumulative effect of both oxidation sequences on the same sample, tensile tests in air at 650°C were performed on non pre-oxidized and pre-oxidized 1 h at 1000°C specimens (Figure 9). More severe oxidation conditions induce not only a loss of alloy elongation to rupture (0.04 against 0.08) but also a reduction of the ultimate tensile strength (-400 MPa). Moreover, SEM observations of fracture surfaces still exhibit intergranular fragile areas. The formation of IOP due to the pre-oxidation treatment at 1000°C in air has no influence on the mechanical rupture mode of studied alloy.

Discussion and Conclusions

Both exposure conditions tested in the present paper leads to intergranular oxidation of alloy 718. Even if atomic oxygen penetrations could have not been clearly identified, high temperature oxidation in air enhances the harmful effects of damage on the mechanical behavior of alloy 718, even for very short time of exposure (10 minutes at 1000°C are enough). The affected depths and local modifications of the chemical composition and microstructure prove the very high sensitivity of alloy 718 to high temperature intergranular oxidation in terms of crack initiation (formation of IOP at 1000°C) and propagation (oxidation assisted intergranular crack propagation at 650°C).

On the one hand, IOP seem not to be critical crack initiation sites. Indeed, tensile test carried on a 1 h at 1000°C pre-oxidized specimen conclusively proves that grain boundaries open after 6% of plastic strain. However, as shown on Figure 6, the effect of oxidation is constant all along the test. So, a possible explanation is that IOP are already opened at the beginning of tensile test but hidden by oxide scale. During the deformation of the specimen, each side of the IOP follows the deformation of a different grain, resulting in a relative displacement which can be regarded as an "opening" of the defect. As IOP are surrounded by hardening precipitates depleted areas, they

blunt themselves under plastic deformation throughout the tensile test, losing in the same time their preferential crack initiation site properties. Nevertheless, if considering Figure 9, the same shift of the tensile curve as the one noticed at room temperature (Figure 6) is observed. As a consequence, the formation of IOP can be regarded as a reduction of effective surface. Furthermore, the loss of alloy elongation to rupture for 1000°C pre-oxidized specimen tends to show that IOP are not only crack initiation sites but also deep enough to locally reach high values of stress intensity factor, hence leading very quickly to rupture. So, they do not immunize alloy 718 from intergranular crack propagation due to oxidation in air at 650°C.

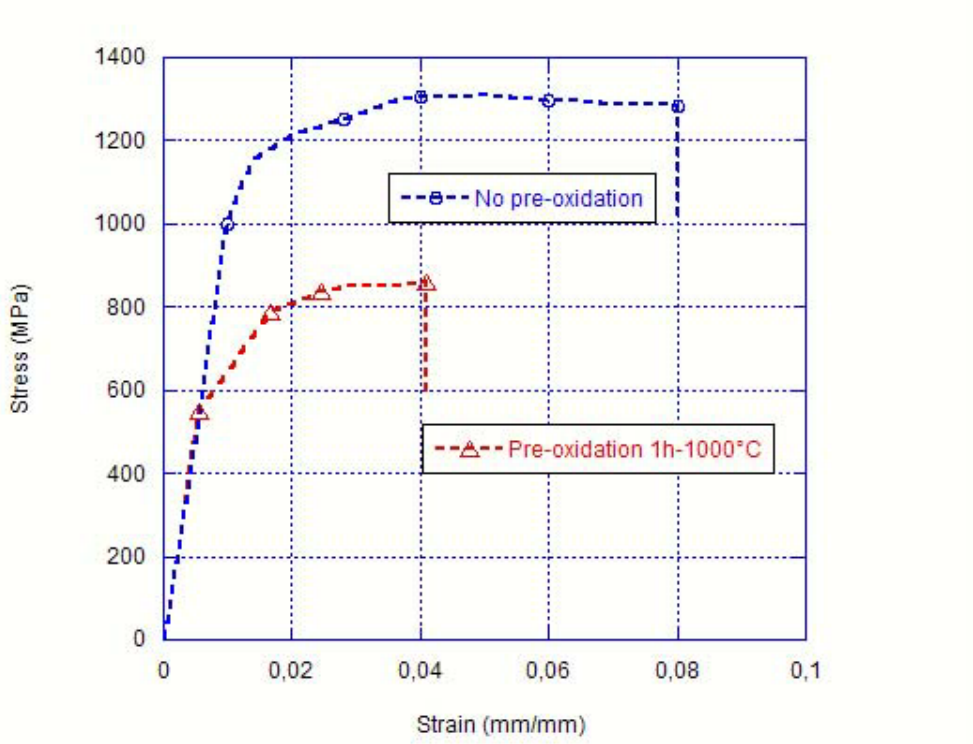


Figure 9: Tensile tests performed at 650°C in air on 1mm thick specimens
(Effect of a pre-oxidation treatment at 1000°C – 1 hour in air).

On the other hand, the tensile tests performed at 650°C in air exhibit the very high sensitivity of rolled products to oxidation assisted intergranular fracture mode. Indeed, this sensitivity is observed all over tested specimens, whatever the surface conditions are. Moreover, several intergranular crack initiation sites are observed on the totality of the gage length of tensile test specimens. The better mechanical properties observed at 650°C in air on non pre-oxidized specimen (Figure 9) can be explained by smaller affected depths in term of IOP (more than 10 µm at 1000°C against 1µm at 650°C), hence lower local values of stress intensity factor. What conclusively proves that oxidation at 650°C can be considered as responsible for intergranular crack propagation is that the same tensile test performed under inert atmosphere leads to a totally transgranular ductile fracture surface. As a result, high temperature oxidation tends to significantly reduce mechanical properties of alloy 718 not only by forming defects such as IOP but also by enhancing crack propagation in an intergranular mode. In addition, very short exposure time to an oxidizing environment is required to induce harmful modifications of mechanical behavior of alloy 718.

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