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To link to this article :

URL : <http://dx.doi.org/10.1016/j.actamat.2004.07.043>

To cite this version : Pérusin, Simon and Viguière, Bernard and Monceau, Daniel and Ressler, Laurence and Andrieu, Eric (2004) *[Injection of vacancies at metal grain boundaries during the oxidation of nickel](#)*. Acta Materialia, vol. 52 (n° 18). pp. 5375-5380. ISSN 1359-6454

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Injection of vacancies at metal grain boundaries during the oxidation of nickel

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Abstract

Nickel foils have been oxidised at 1000 °C on one side only in laboratory air, the other side being protected from oxidation by a reducing atmosphere. After the oxidation treatment, the unoxidised face was carefully examined by using an atomic force microscope. Grain boundaries grooves were characterised and their depth were compared to the ones obtained on the same sample heat treated in the reducing atmosphere during the same time. Grain boundaries grooves are found to be much deeper in the case of the single side oxidised samples. It is shown that this additional grooving is directly linked to the growth of the oxide scale on the opposite side and that it can be explained by the diffusion of the vacancies produced at the oxide scale–metal interface, across the entire sample through grain boundaries. Moreover, the comparison between single side oxidised samples and samples oxidised on both sides points out that voids in grain boundaries are only observed in this latter case proving the vacancies condensation in the metal when the two faces are oxidised.

Keywords: Nickel; Nickel Oxide; Vacancy Injection; Voids; Grooves; AFM

1. Introduction

Theory of oxidation of metals developed by Wagner [1] envisages the diffusion of one or more reactants through an oxide scale which covers the surface of a semi-infinite metallic substrate. When an oxide grows by the outward diffusion of cations, fresh oxide is formed at the gas–oxide interface whilst metal atoms enter the oxide layer as metal ions at the metal–oxide scale interface. Vacancies are then created in the metal lattice at the metal–oxide scale interface. This phenomenon is well accepted but the destiny of metal vacancies is subject to debate and two types of models are well docu-

mented in the literature. The first one considers that vacancies diffuse in the metal lattice until they are annihilated at sinks (not always well defined) such as grain boundaries, voids, impurities or dislocations [2–17]. This process was called vacancy injection by Dunnington [2] in 1952. The presence of voids in the bulk of oxidised metals is then explained by the condensation of these vacancies. The second family of models assumes that vacancies remain at the metal–oxide scale interface where they form voids [9,13,18] if the oxide is not ductile enough to maintain a good contact with the metal [9,19] or are annihilated by the climb of misfit dislocations [20,21]. If vacancies are annihilated at the metal–oxide scale interface, the presence of voids observed in the metal after oxidation is explained by the formation of carbon dioxide by the reaction between solute carbon and oxygen diffusing into the metal [22–26].

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The question of the mobility of vacancies in the metal is then asked: could they cover a long distance or not before being annihilated?

To answer this question, polycrystalline nickel foils were oxidised on one side only, the other side being protected from oxidation. Then a careful examination of the unoxidised surface was carried out. The original guiding idea of the present work is based on that of Francis and Lees [15] who oxidised thick iron disks on one side and showed some interesting specific features related to these unusual oxidation experiments. In the present study, single side oxidation experiment is combined with atomic force microscope (AFM) analysis to attempt a quantitative analysis of the vacancy injection phenomenon. Special attention is paid to grain boundaries behaviour.

2. Material and experimental procedures

The investigations were conducted on annealed high purity (99.98%) nickel foils (Table 1), 125 μm and 1 mm thick. The mean grain size of the as received materials is around 50 μm for the 1-mm thick foil and 35 μm for the 125 μm thick foil. Surface preparation is well known to play a great role on the oxidation kinetics and on oxide morphologies [27,28]. Surfaces of the foils were then carefully polished down to 1 μm using diamond paste. Specimens were then electrolytically polished on one side by a mixture of 2/3 perchloric acid and 1/3 acetic acid at room temperature under 70 V for 5 s. The faces were then degreased in acetone and ethanol and the electropolished face was characterized using AFM technique: the roughness R_t was estimated to be less than 50 nm and no grain boundary dissolution was observed. After cleaning, the foils were annealed in a dry mixture of argon and hydrogen (5 vol% H_2) at 1000 $^\circ\text{C}$ for 1 h in order to stabilize the microstructure. The mean grain size obtained after heat treatment was in the range 350–450 μm for the two types of foils.

The experimental oxidation device (Fig. 1), inspired from Francis and Lees [15], consists of a superalloy hollow cylinder chamber on which the foils are placed and blocked with a superalloy hoop. One side of the specimens was oxidised (the side which was not electrolytically polished) by laboratory air whereas the opposite side was exposed to an argon and hydrogen mixture (Ar–5 vol% H_2 under 1.2×10^5 Pa pressure) to protect it against oxidation (protection which was confirmed

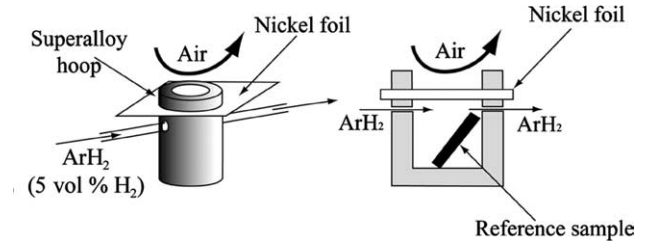


Fig. 1. Setup used for the oxidation of nickel foils on one side: general view and cross-section of the experimental device.

by X-ray Photoelectron Spectroscopy analysis). A reference coupon with both faces prepared following the procedure defined for the samples oxidised on one side, was put inside the chamber so that it was entirely protected from oxidation (see Fig. 1).

Two oxidation treatments were given: 15 h at 1000 $^\circ\text{C}$ for the thinnest foil and 48 h at 1000 $^\circ\text{C}$ for the thickest one. After disassembling carefully the pile-up, a detailed examination of the unoxidised surfaces, and particularly of the grain boundaries intercepting the inert surface, was performed using AFM. For this purpose, a Nanoscope IIIa Atomic Force Microscope of Digital Instruments[®] was used in tapping-mode, in ambient air, using a silicon tip characterized by a 5 nm nominal radius of curvature, a 35 $^\circ$ interior angle and a height of 15 μm .

A Leo 435 VP SEM was also used to examine the surface protected from oxidation and the cross-section of the thickest foil oxidised on one side.

3. Experimental results

3.1. Grain boundary grooving in single side oxidised sample

For the Ni/NiO system, the oxide scale–metal adhesion is recognised to be excellent for flat surfaces [29–31]. Indeed, we did not observe any spallation neither on specimens oxidised on one side nor two sides. The thickness of the NiO scale is about 15 μm after 15 h at 1000 $^\circ\text{C}$ and 35 μm after 48 h which is in a quite good agreement with previous results [32–34]. The oxide scales were observed after electrolytic dissolution of nickel in a diluted nitric acid solution (50 vol% HNO_3) during 5 min at 4 V. In each case, the scale consists of an inner layer of equiaxed grains showing

Table 1
Chemical composition of the nickel foils

Component	Co	Cr	Cu	Fe	Mg	Mn	Si	Ti	C	S	O	N	Ni
Concentration (at. ppm)	8	9	9	11	24	11	17	12	10	0.7	4.4	0.08	Bal

few voids and a compact outer layer of columnar grains. The thickness ratio R ($R = \text{outer layer/inner layer}$) is about 1.5 whatever the treatment duration (Fig. 2). As illustrated in Fig. 3, the surface of the foil protected from oxidation shows grain boundaries grooves that look like the ones observed in the reference sample. On the AFM view, one can easily recognize three grain boundaries intercepting the surface of the metal. Fig. 4 shows another example of an AFM top view and the corresponding section of the surface exposed to the reducing atmosphere. In the following section, results obtained for the samples oxidised on one side are compared with the ones achieved for the reference samples.

3.2. Comparison between samples oxidised on one side and reference samples

It is well known that thermal grooves develop on the surface of a hot polycrystal wherever stationary grain boundaries emerge to intersect the surface. This thermal effect was called “thermal grooving” by Mullins [36] in 1957. The usual condition for the equilibrium was given by Bailey et al. [37] for a gas–solid interface

$$2 \times \gamma \times \cos\left(\frac{\psi}{2}\right) = \gamma_b, \quad (1)$$

where γ and γ_b are, respectively, the surface and grain boundary energies per unit area.

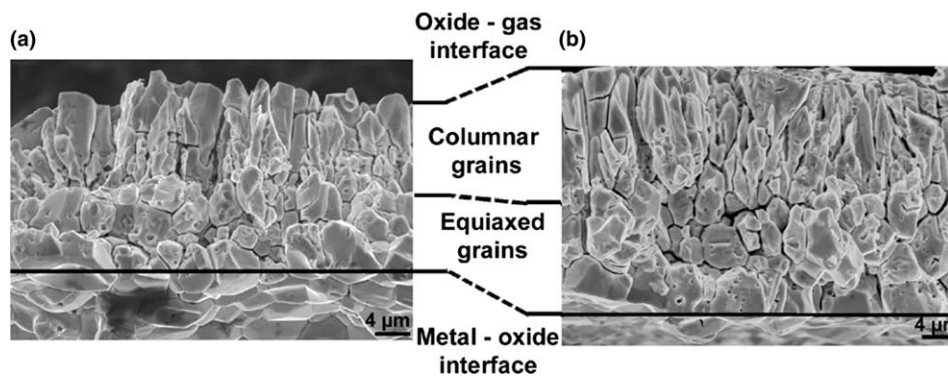


Fig. 2. Duplex microstructure of NiO formed on nickel after heat treatment in laboratory air: (a) 15 h at 1000 °C; (b) 48 h at 1000 °C – tilted view.

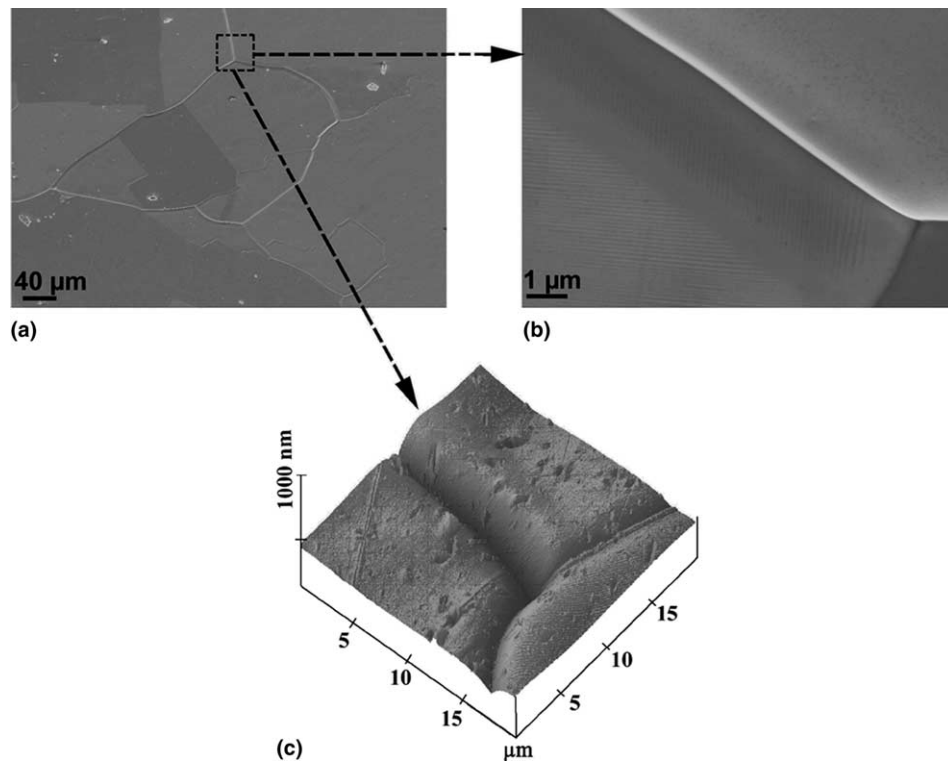


Fig. 3. (a,b) Surface of the foil protected from oxidation observed with the SEM and (c) corresponding topography obtained with the AFM (15 h at 1000 °C).

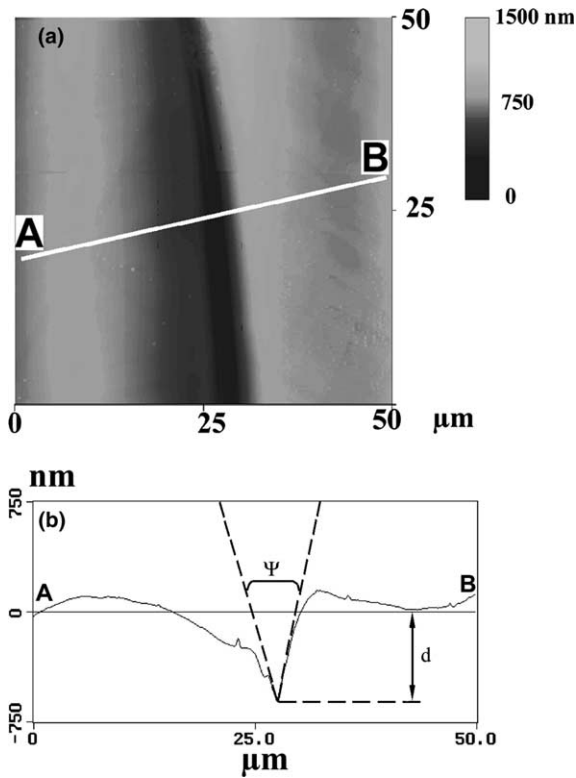


Fig. 4. AFM top view (a) and the corresponding section (b) of the surface protected from oxidation (15 h at 1000 °C).

AFM is an accurate technique to measure the depth d and the angle Ψ at the tip of the grooves as defined in Fig. 4, as recently used to study the geometry of grain-boundary grooves in polycrystalline alumina [38]. Measurements of d and Ψ have been made for the nickel foil (125 μm thick) oxidised on one side and for the reference foil with both sides annealed in Ar–5 vol% H_2 . The re-

sults obtained for the samples treated 15 h at 1000 °C (the thinnest foil), are presented in Fig. 5. This figure points out first that the angles of the grooves are quite the same for the single side oxidised specimens and for the references. Using the equilibrium equation of Bailey (Eq. 1) and assuming the ratio $\gamma_b/\gamma = 1/3$ according to McLean and Murr [39,40], one finds that the angle of the groove at 1000 °C for pure nickel is about 161° which is close to the mean value 158° found for the two types of samples. But the most striking and interesting result is the fact that grooves are much deeper for the samples oxidised on one side only (Fig. 5(a)) than for the reference sample. The difference between the mean depth values is indeed around 300 nm which represents a volume of 2.3 μm^2 per unit length of grain boundary.

3.3. Thick specimens oxidised on one side and on both sides

Cross-sections of the thickest foils (1 mm thick) oxidised on one side 48 h at 1000 °C were made and SEM observations were compared with the ones obtained for the same specimen oxidised on both sides. The NiO scale thickness is around 35 μm in both cases and, as illustrated in Fig. 6, the metal oxidised on both sides show many voids localised at the grain boundaries contrary to the sample oxidised on one side in which grain boundaries are particularly clean. These voids did not exist in the as-received materials and since the chemical composition of the two samples are exactly the same, with a low carbon content, the observed voids cannot be attributed to the formation of CO or CO_2 as suggested in [22–26]. Image analysis was used to calculate the mean size \bar{w} and the volume fraction f_v of the voids (assuming that the volume fraction f_v is equal to the surface fraction f_s). \bar{w} was found to be about 10 μm and f_v about 0.01%.

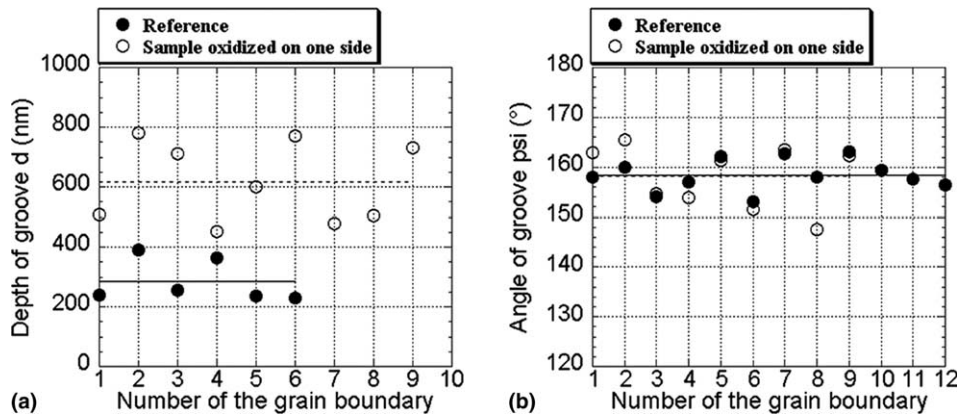


Fig. 5. Comparison of depth d (a) and angles Ψ (b) of grooves between samples (125 μm thick) oxidised on one side and references (the mean values are represented by solid lines for the reference and by dash lines for the sample oxidised on one side) – 15 h at 1000 °C. The diameter of the discs represents the amplitude of the experimental uncertainties (2° for the angle and 30–40 nm for the depth).

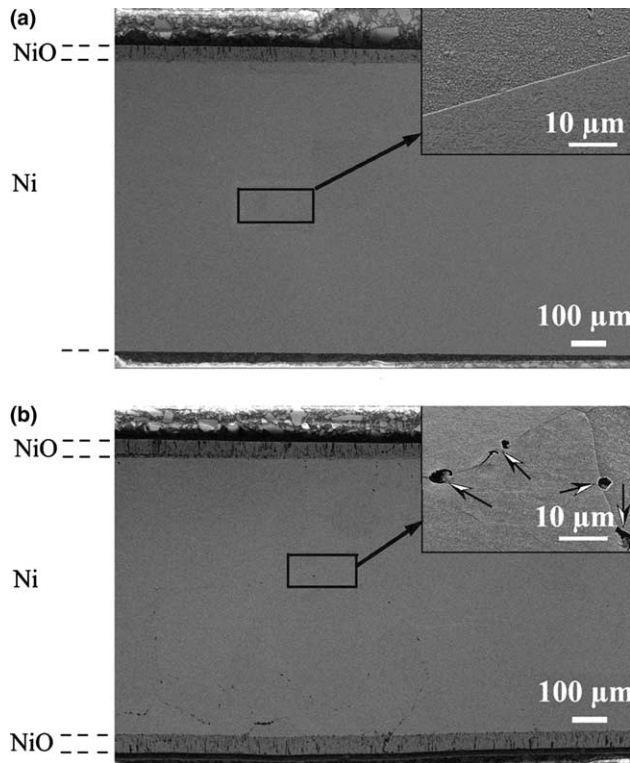


Fig. 6. High purity nickel sheets (1 mm thick) oxidised: (a) on one side; (b) on both sides – 48 h at 1000 °C – laboratory air – detailed observations of the grain boundaries shown in insert reveal the presence of numerous voids (see arrows) only in the specimen oxidised on both sides.

4. Discussion

If each metal atom used to build the oxide scale would produce a vacancy and if all these vacancies were injected and not annihilated, this would give an additional vacancy concentration in the metal bulk of

$$C'_v = \frac{t_{ox}}{\phi \times t_m}, \quad (2)$$

where t_{ox} is the scale thickness, t_m the initial thickness of the coupon (125 μm in our case) and ϕ the Pilling and Bedworth ratio ($\phi = 1.65$ for the Ni/NiO system [41]). The fact is that all the produced vacancies are not injected: some of them may be annihilated by the interface motion. The examinations of the oxide scales formed under the present conditions revealed a duplex micro-structure with an inner layer of equiaxed grains and an outer layer of columnar grains (Fig. 2). As demonstrated by Peraldi et al. [35], the interface between inner and outer scales marks the initial metal surface. Thus, considering a Pilling and Bedworth ratio of 1.65 for the NiO/Ni system, the thickness ratio R between the outer scale and the inner scale should be equal to 0.61 if all the cation vacancies were annihilated by the interface motion and ∞ if they were all injected. The measured ratio of $R = 1.5$ corresponds to the injection of 34% of all the

potential vacancies. Indeed, for 1 vol. unit of metal consumed by the oxidation process, 1.65 vol. of oxide is formed. As the equiaxed internal layer constitutes 2/5 of the total oxide scale, the volume of non annihilated vacancies is: $\Delta = 1 - (2/5) \times 1.65 = 0.34$. On the one hand, if those injected vacancies would remain in the metal bulk without being annihilated, the additional vacancy concentration would be

$$C_v = 0.34 \times \frac{t_{ox}}{\phi \times t_m}. \quad (3)$$

After 15 h at 1000 °C, t_{ox} is equal to 15 μm giving a value of 2.47×10^{-2} for C_v which is much higher than the known equilibrium vacancy concentration C_v^{eq} in nickel at 1000 °C, i.e., 7×10^{-4} [42].

On the other hand, if all those vacancies would run across the entire thickness of the specimen and condense at the grain boundaries intersecting the non oxidised surface, they would groove the grain boundaries by 594 μm^2 per unit length (assuming tetragonal grains of side 230 μm). That the experimental grooving (2.3 μm^2) represents 0.38% of the maximum value. The remaining injected vacancies (i.e., most of them) are then expected to be annihilated either close to the metal–oxide scale interface (e.g., by the climb of misfit dislocations [21]) or in the bulk (e.g., by restoration mechanisms or by the formation of vacancy loops [5]).

Concerning the presence of voids in nickel, the comparison between single side oxidised sample and sample oxidised on both sides points out that voids are only observed in this latter case and are located at grain boundaries. These voids cannot be formed during the cooling of the sample since no voids are observed in the single side oxidised sample. Moreover, since cavities can arise from creep damage, it has been verified that the specimens do not creep under those experimental conditions: nickel specimens (125 μm and 1 mm thick) have been hung up in a furnace and the changes in the dimensions of the samples due to the oxidation treatment were followed using a laser extensometer; the maximum measured strain was lower than 5×10^{-4} . Thus, these voids are neither due to chemical effects nor creep damage; they are believed to be a proof of the vacancy injection phenomenon.

In the case of a sample oxidised on one side, the non oxidised metal face constitutes a perfect sink for annihilation of vacancies which diffuse from the metal–oxide scale interface to it. In the case of a sample oxidised on both sides, vacancies are injected in the metal at both sides of the sample, leading to the formation of voids. Volume fraction of the observed voids (0.01%) corresponds to 0.66% of the total number of injected vacancies which turns out to be close to the value found to explain the deeper grooves formed in single side oxidised samples ($2 \times 0.38\%$).

The observation of deeper grooves measured for the samples oxidised on one side and the observation of voids at grain boundaries in the sample oxidised on both sides far from the metal–oxide scale interface are consistent with the idea that grain boundaries do not constitute perfect sinks for vacancy annihilation but fast diffusion paths. The data scatter evidenced in Fig. 5(a) can be attributed to the different paths followed by the vacancies (it depends on the length and the nature of the grain boundaries).

5. Conclusions

Detailed observations made on samples of nickel oxidised on one or both surfaces have shown that some of the vacancies formed during oxidation are injected in the metal and generate: (a) voids in the metal when the two faces of the substrate are oxidised; (b) additional grain boundaries grooves on the unoxidised surface in the case of single side oxidised samples.

A quantitative analysis of the grain boundary grooves and of the volume fraction of voids shows that the number of vacancies annihilated in voids or at the unoxidised surface is a small proportion of the total amount of produced vacancies. Then, classical mechanisms of vacancies annihilation such as dislocation climb or formation of vacancy loops have to be taken into account. Nevertheless, the number of vacancies that are shown to diffuse over large distances through grain boundaries remains large enough to strongly influence mechanisms responsible for mechanical properties, such as dislocation climb and grain boundary diffusion and sliding.

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