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What If the Protection against Oxidation of Chromia-Forming Alloys Was Not Always Due to the Chromia Layer?

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Abstract

Chromia-forming alloys have good resistance to oxidizing agents such as O_2, CO_2, … It is accepted that the protection of these alloys is always due to the chromia layer formed at the surface of the alloys, which acts as a barrier between the oxidizing gases and the alloy substrates, forming a diffusion zone that limits the overall reaction rate and leads to parabolic kinetics. But this was not verified in the study devoted to Inconel®625 the oxidation in CO_2 that was followed by TGA, with characterizations by XRD, EDS and FIB microscopy. Contrary to what was expected and accepted in similar studies on other chromia-forming alloys, it was shown that the diffusion step that governs the overall reaction rate is not located inside the chromia layer but inside the alloy, precisely inside a zone just beneath the interface alloy/chromia, this zone being depleted in chromium. The chromia layer, therefore, plays no kinetic role and does not directly protect the underlying alloy. This result was demonstrated using a simple test that consisted in removing the chromia layer from the surface of samples partially oxidized and then to continue the thermal treatment: insofar as the kinetics continued without any change in rate, this proved that this surface layer of oxide did not protect the substrate. Based on previous work on many chromia-forming alloys, the possibility of a similar reaction mechanism is discussed. If the chromia layer is not the source of protection for a number of chromia-forming alloys, as is suspected, this might have major consequences in terms of industrial applications.

Keywords

Chromia-Forming Alloys, Chromia Layer, Oxidation Protection, Inconel®625, Kinetics

1. Introduction

Chromia forming alloys, such as Ni-Cr based, are well known for their high temperature oxidation resistance [1]. Widely used in the petrochemical, aerospace and nuclear industries, these alloys have a long service life in corrosive gases, including mainly oxygen but also other oxidizing gases as water or carbon dioxide [2] [3].

The chromia layers formed at the surface of these alloys, from the very beginning of their use, are generally considered to be responsible for their good behavior. The reaction mechanism usually involved implies that the reaction rate was governed by the slow diffusion of the species through the chromia layer, the limiting step being either the inward diffusion of oxygen ions (from air or other reactive gases), or the outwards diffusion of chromium ions [4] [5]. The role of the semi-conduction of Cr_2O_3 was extensively studied, particularly because this can have a kinetic impact, and because the semi-conduction may change according to the presence of impurities or even according to the level inside the layer (p-type at the outer surface or n-type close to the substrate [5]).

Factually, and even if the protective character of the chromia layer is never discussed, this schematic reaction mechanism is not exactly followed in many cases, depending on the duration of the treatment (the other components of the alloys always react for long exposure times [6]), the nature of the alloy [7] [8] and the reacting gases, in particular in presence of water [9]. The role of titanium was also underlined because, when it is present in the alloys, even as simple traces, it oxidizes simultaneously with chromium, and it may modify the kinetics [10].

Otherwise, the influence of the Cr percentage in the alloys has been reported in many studies [11], but the actual function of the resulting oxide layer has never really been discussed, its role as diffusion barrier always being directly admitted.

Now, a recent article devoted to the Inconel®625 oxidation in CO_2 [12] highlighted another reaction mechanism to justify the oxidation resistance of this alloy. This article brought to the fore that the diffusion of species through the chromia layer is not the limiting step and that, in this case, the dense chromia layer formed plays no kinetic role at least at the start of the reaction.

Following on from this latest study, the present article focuses on the chromia layer formed during the dry corrosion of chromia-forming alloys, in the specific case of the Inconel®625 corrosion in CO_2 by detailing how it was established that the chromia layer was not protective in this case. Going further, the case of other chromium alloys is analyzed based on previous studies, in the light of these new results.

2. Experimental Materials and Method

2.1. Material

Inconel®625 was in the form of small discs, 12 mm in diameter and 2 mm thick, made from commercial sheets provided by Goodfellow Inc. (England). Inconel®625 was mainly composed with 59.5 wt%, 21.5 wt% and 9 wt% of nickel,

chromium and molybdenum respectively.

The gases used were provided by Air Liquide, France, with N45 quality for CO_2, Alpha 1 for Argon and Alpha 2 for helium. Their main impurities were water and oxygen [12].

2.2. Thermogravimetry

Oxidation kinetics experiments were carried out, in the temperature range of 1173 to 1273 K, by using a Thermobalance type SETSYS Evolution (Setaram S.A., France). The zero time of each kinetic curve was determined within only a few seconds by moving the sample in the middle of the furnace, when the required temperature was reached (with the heating rate of 20˚C/min). Usually, the treatments lasted 10 h, and the samples were then quenched by moving to the cold zone of the furnace.

2.3. Characterizations

Cross-section observations were carried out with a Zeiss Crossbeam 550 FIB microscope using a probe current of 750 pA under 3 kV. Micrographs were obtained with the optical microscope Nikon Eclipse LV100 and with the SEM JEOL IT300 working under 10 kV, equipped with a silicon-lithium detector for the EDS analyses.

3. Experimental Results and Discussion

3.1. Behavior of Inconel®625 in CO_2 and Reaction Mechanism

It is necessary to recall some of the characteristics of the oxidation of Inconel®625 since this is the basis of the present study. The main elements of this work are first reviewed and then completed, before presenting the original method used to determine the role of the chromia layer in the case of Inconel®625 oxidation, and before extending the study to the case of other chromia-forming alloys.

3.1.1. Experimental

Inconel®625 discs were placed in flowing CO_2 leading to parabolic kinetics for durations of less than 10 h [12]. **Figure 1** provides the linear representations of the TGA in coordinates $(\Delta m/S)^2$ vs. time t, where $\Delta m/S$ is the mass increase per surface unit.

The influence of the gas pressure on the reaction rate was tested by changing the CO_2 flow, which had not any kinetic effect. Furthermore, this study showed that the kinetic behavior of Inconel®625 in CO_2 was similar to that observed in air or oxygen, even at very low pressures obtained using inert gases containing just traces of oxygen (Ar and He, with 2 and 0.2 ppm O_2, respectively), see **Figure 2**. The slight differences observed were attributed to experimental uncertainties and to the Archimedean thrust.

In line with thermodynamic studies which show that chromium oxidizes before the other major components of the alloy and that chromia Cr_2O_3 is the only oxide stable for P_{O2} higher than about 10^{-3} Pa at the considered temperatures [12], the

only product of the reaction found was chromia, but containing some traces of titanium, this element being present but only in very small quantity in the alloy used (<0.25 wt%).

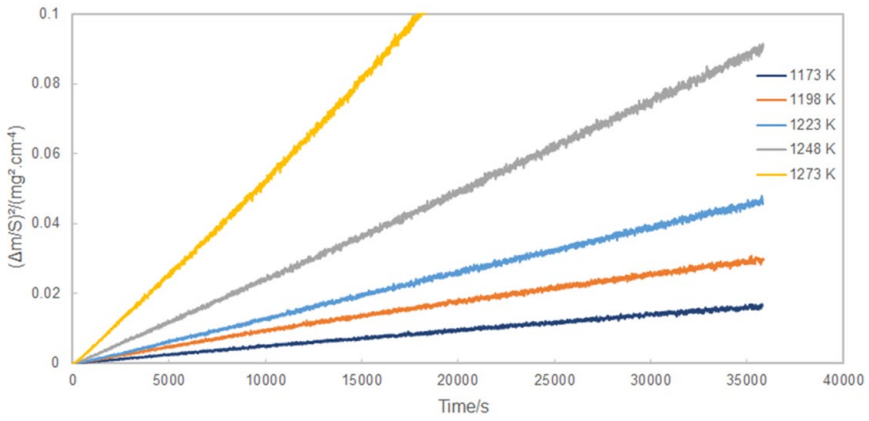

Figure 1. Linear representation of the square of the mass increase per surface unit (Δm/S) of Inconel®625 oxidized in flowing CO_2 (20 L·min^{-1}) according to time [12].

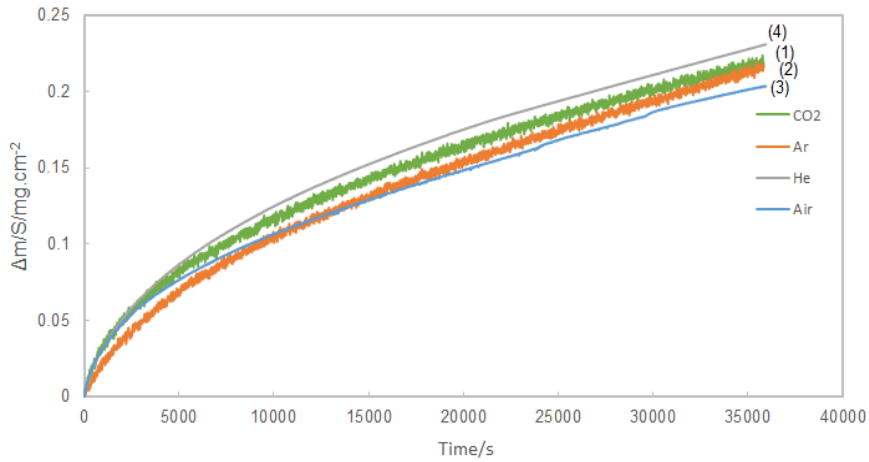

Figure 2. Kinetics obtained at 1223 K showing that the nature of the gases used, and the oxygen pressure have no appreciable effect on the reaction rate: (1) CO_2; (2) Ar (3) air; (4) He [12].

The thickening of the chromia layer occurred via external growth, which was established by the platinum marker test [12]. This means that chromium ions crossed the oxide to form the chromia lattice at the external surface of the chromia layer.

The oxide, therefore covered the samples, forming a layer of rather irregular thickness, but without the spalling areas often seen in similar systems. The irregularities in the chromium layer are clearly visible on the FIB micrograph (Zeiss Crossbeam 550) in **Figure 3**. This image also shows the polyhedral grains of the underlying alloy, but mainly the formation of a significant porosity, visible even deep inside the alloy up to more than 10 μm, and also the presence of grains clearer, close the interface with the oxide layer.

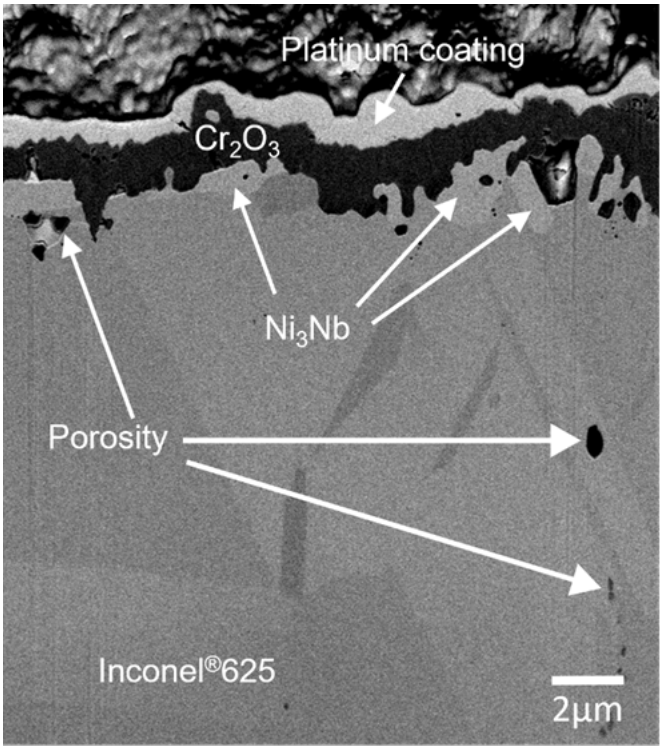

Figure 3. FIB micrography of a cross-section of the alloy oxidized 15 h in flowing CO_2 at 1223 K.

The EDS cartographies in **Figure 4(a)** and **Figure 4(b)** show that these grains are very rich in niobium, while the XRD analysis in **Figure 4(c)** reveals small peaks identified as corresponding to the Ni_3Nb phase that were not observed in the initial alloy. It was therefore concluded the grains that accumulated close to the alloy/oxide interface were composed of the Ni_3Nb intermetallic; they are characteristic of oxidized Inconel®625 [13], being initially present everywhere in the bulk of this alloy but, after oxidizing, gathered in quantities at the interface oxide/alloy.

The last important point to understanding the reaction mechanism is the Cr-depletion profile observed inside the oxidized alloy, which was characterized by the EDS analysis of a cross-section (SEM JEOL IT300 equipped with a silicon-lithium detector) and reported in **Figure 5**: this Cr-depletion proves that chromium drawn from of the alloy to form the oxide layer was not immediately replaced by atoms coming from the core of the alloy *i.e.*, that the alloy close to the interface with the oxide layer constitutes a diffusion zone.

3.1.2. Reaction Mechanism and Role of the Chromia Layer

The reaction mechanism necessarily implies a limiting diffusion step, in order to justify the parabolic kinetics. However, there are two possibilities:

1) The diffusion of point defects inside the chromia layer (evidenced by the external growth of the chromia layer).

2) The diffusion of chromium atoms inside the Cr-depleted zone of the alloy (proved by the Cr profile of **Figure 5**).

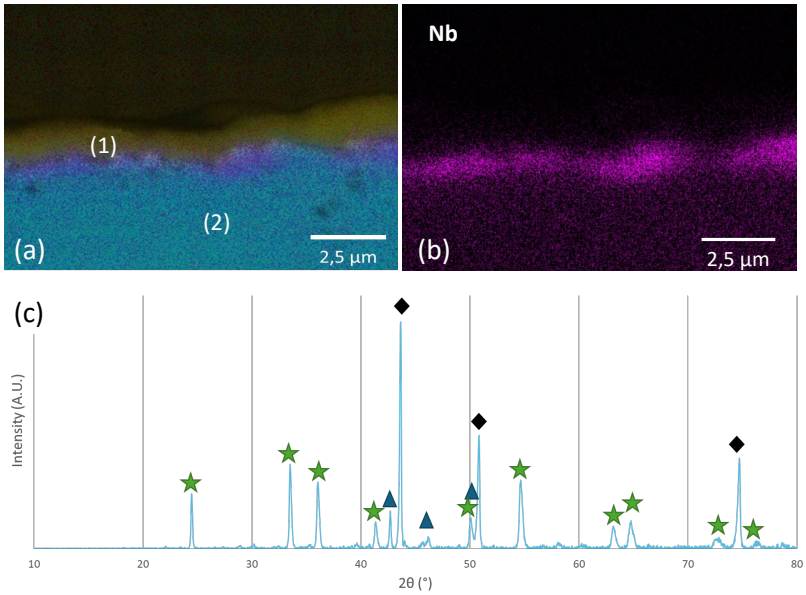

Figure 4. Microanalysis of Ni_3Nb intermetallic grains after 10 h-oxidation at 1000˚C: (a) general cross-section of the interfacial zone with oxide (1) and alloy (2); (b) the corresponding EDS mapping of Nb; and (c) the XRD patterns of the surface of the sample showing the Ni_3Nb peaks (triangles) at 43.67˚, 46.14˚ and 50.03˚, according to the JCPDS file n˚00-017-0700, together with the peaks of chromia (asterisks) and of the substrate (diamonds).

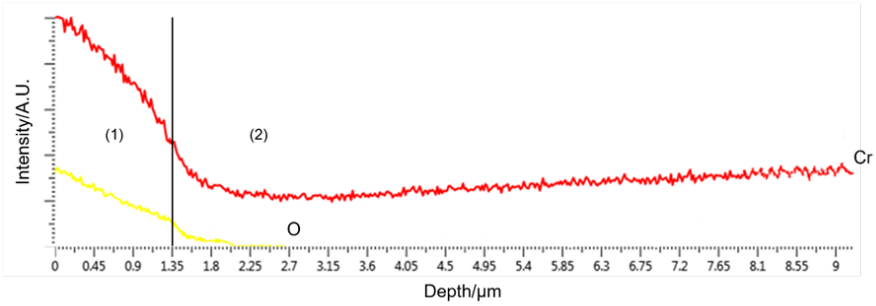

Figure 5. Chromium profile inside Inconel®625 oxidized 10 hours in flowing CO_2 at 1223 K, going from the oxide layer (1), left part, to inside the alloy (2), right part.

If the diffusion within the oxide is limiting, the semi-conduction of Cr_2O_3 must be considered because the reaction mechanism is different depending on whether the oxide is an n-type or p-type semiconductor [14] and, in particular, the pressure of the reactive gas must influence the reaction rate if the oxide is a p-type semiconductor. But this question of semi-conduction in chromia is controversial because, depending on the experimental conditions and the nature of the traces of impurities, chromia can be either an n-type or a p-type semiconductor [5].

Factually, it is possible to overcome this difficulty by using a very simple experiment consisting in removing the oxide layer from the sample surface, which easily allows determining the localization of the limiting step: if it is located inside the chromia layer, hence this layer protects the underlying alloy and, when removed, the reaction must restart. If the reaction does not restart, this means that the

chromia layer does not play any kinetic role and, consequently, that the diffusion limiting step is located inside the Cr-depleted zone of the alloy.

This method, which appears both very simple in principle and very demonstrative, has never been applied to chromia-forming alloys, as far as we know, and that is why it seemed necessary to detail this method in the following section: this is an essential part of this article.

Concerning the oxidation of Inconel®625 in flowing CO_2, after removing the oxide layer the reaction continues without any rate change (see the following section), which proves that the limiting step was located inside the alloy, and not inside the oxide layer.

The reaction mechanism can, therefore, be described as follows, moving from the oxide surface towards the inner alloy [12], without any consideration about the nature of semi-conduction in chromia:

1) Sorption of CO_2 and reaction with chromium at the surface of the oxide.

2) Diffusion of the point defects in chromia.

3) Interface reaction at the surface of the alloy (transformation of chromium atoms Cr into ions Cr^{3+}) causing the impoverishment in chromium of the alloy close to the oxide layer. This transfer of chromium from the alloy to the oxide layer creates atoms vacancies in chromium inside the alloy.

4) Inward diffusion of the chromium vacancies inside the alloy zone close to the oxide layer (*i.e.*, outward diffusion of chromium atoms). This step is slow, necessarily slower than the other steps, so it constitutes the limiting step of the overall reaction. This outward migration of chromium may pull grains of Ni_3Nb initially present inside the alloy, justifying that these grains progressively gather at the interface alloy/oxide, as seen in **Figure 3**.

5) The chromium vacancies gather, perhaps along grain boundaries of the alloy, and locally create pores even deep inside the alloy, as observed in **Figure 3**.

It is worth noticing that this chain of reactions is often admitted for the beginning of the oxidation of chromia forming alloys, before that the other component of the alloys oxidize in turn. However, in the initial stage of such reactions, the limiting step was never considered to be located inside the alloys, which is the opposite of what is described here.

This point is interesting from the theoretical point of view, but not only. Indeed, in the numerous applications where the alloys undergo mechanical stresses, if the oxide layer does not play any protective role, it does not matter whether the oxide layer remain linked to the underlying alloy, or not. It is exactly the same about spallation: if it occurs, it diminishes the oxide layer thickness, but this has no impact on the lifetime of the alloy. This might open new fields for the use of Inconel®625 that is sometimes rejected because of the lack of adherence of the oxide layer, supposed protective.

3.2. Details and Interest of the Surface Oxide Layer Removal Test for Chromia-Forming Alloys

Two experimental methods can be used to remove the surface oxide. They are

detailed below, using as an example the removal of the chromia layer formed during the oxidation of Inconel®625 in CO_2, which is detailed above.

3.2.1. Removal by Polishing

The first method used consists of a simple polishing of the surface with SiC paper (grade 1200). This method has the advantage of being easy to implement. But very often, with chromia-forming alloys, the interfaces oxide/substate are very irregular (as seen in Figure 3 and as roughly illustrated in Figure 6(a)). In this case, either traces of the surface oxide layer remain attached to the substrate (if polishing is insufficient, as shown schematically in Figure 6(b)), or the substrate is etched (when polishing is too thorough, as shown schematically in Figure 6(c)).

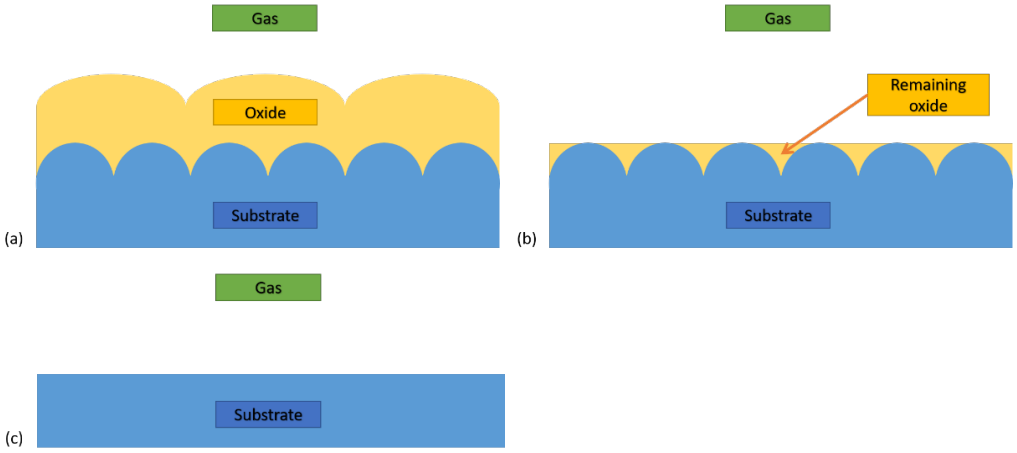

Figure 6. Schemes showing the effect of polishing on the removal of the surface layer of chromia formed on chromia-forming alloys. (a) Schematic cross-section of the partially oxidized alloy; (b) after the light polishing leaving traces of oxide at the surface and (c) after the too-hard polishing having attacked the alloy.

In fact, if the aim of this test is to prove that the oxide layer does not protect the substrate, the first case (polishing too lightly) could be considered sufficiently demonstrative: after having replaced the so-polished sample inside the thermobalance, if the reaction continues without rate change, this alone proves that the oxide layer was not protective. Indeed, if the simple thinning of the oxide layer has not any kinetic effect, this shows that this layer was not the place of the limiting step of the reaction. If the reaction starts up again, even just a little, this means that the oxide layer was protective, and that the limiting diffusion step occurs inside this layer.

On the opposite, if the polishing attacks the substrate (Figure 6(c)), this must lead to an acceleration of the rate in every case: if the oxide layer protects the alloy, its removing result in the restart of the reaction, and if the limiting step is located inside the alloy, the thickness of the diffusion zone is reduced, and this entails the increasing of the reaction rate.

It should also be noted that polishing requires the samples to be removed from the oven and cooled to room temperature before being heated again. This can

result in spallation or even the detachment of the oxide layer from the substrate if the bonding of the oxide to the substrate is insufficient and/or if the coefficients of thermal expansion of the substrate and oxide are significantly different (which is often the case). Consequently, it is necessary to verify that the kinetics are not modified by the cooling and the re-heating of the samples. This test is relatively simple to implement and should be carried out.

Figure 6 presents all the results obtained in the case of Inconel®625 oxidation in CO_2. Figure 7(a) presents the optical micrograph, obtained with the optical microscope Nikon Eclipse LV100, of the surface of a sample oxidized for 10 hours at 1223 K and then polished in order to remove the oxide layer. Actually, since the oxide layer is very thin (about 2 µm, see Figure 3) and the interface being rather irregular, the polishing easily could be not complete, as illustrated in Figure 7(a) where the remaining traces of oxide are the clear zones. This corresponds to the case schematically illustrated in Figure 6(b), but here the asperities of the alloy/oxide interface are so pronounced that the alloy itself could have been partially etched in places. Nevertheless, the kinetics in Figure 7(b) clearly show that the removal of the oxide had virtually no effect on the reaction rate, as explained in detail below, looking at each curve in Figure 7(b).

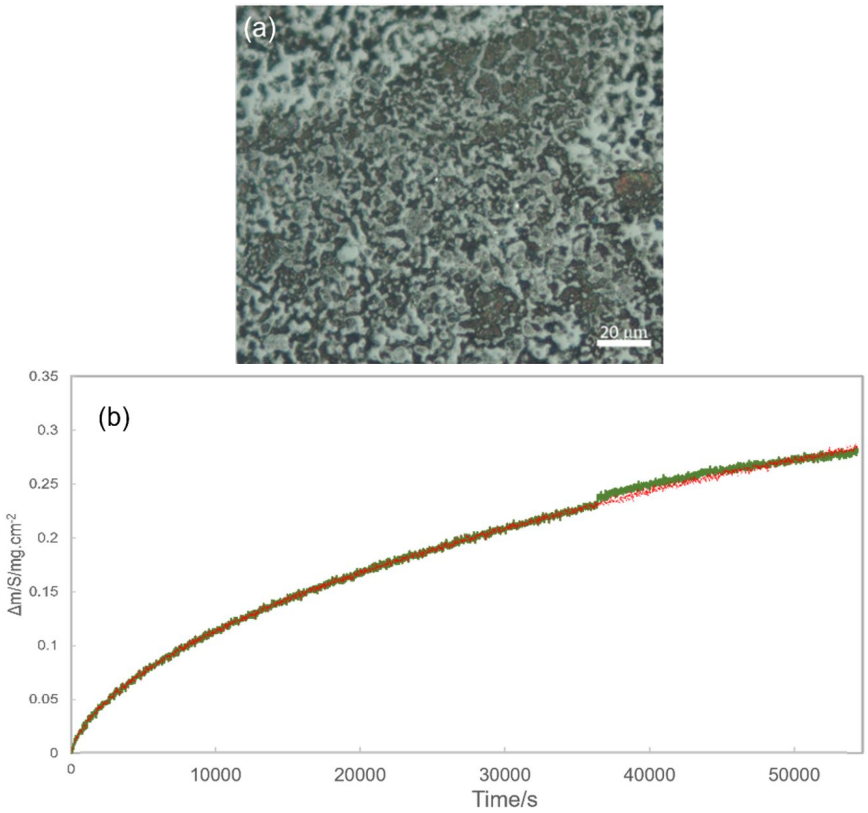

Figure 7. Polishing of the partially oxidized Inconel®625 at 1223 K in CO_2 and re-oxidizing. (a) Aspect of the surface after polishing and (b) the corresponding kinetics: in blue, the curve obtained with a 10-hour heating (confused with the red curve); in red, the curve obtained with a direct 15-hour heating; in green, the curve obtained with a 10-hour heating, then polishing the sample, and then re-heating for 5 extra hours.

First, the verification that the thermal cycle does not affect the kinetics: the blue curve in **Figure 7(b)** is obtained by simply heating for 10 hours and the red curve is obtained by heating for 10 hours, then cooling, and finally heating again for 5 hours. The red curve is superimposed on the blue curve for the first 10 hours (360,000 s) and is in perfect continuity with the blue curve for the next 5 hours, which means that the thermal cycle has no kinetic effect.

Next, the determination of the polishing effect: a sample was polished as described above, as shown in **Figure 7(a)**, and then treated again at 1223 K: the green curve then obtained is almost superimposed on the red one, the slight restart observed being attributed to the slight etching of the substrate mentioned above.

This clearly demonstrates that the oxide layer formed on the surface of the partially oxidized Inconel®625 does not protect the underlying alloy since, when it is removed, the kinetics continues as before.

3.2.2. Removal by Ion Beam Etching

It is also possible to remove the chromia layer by ion beam etching. The apparatus used was a GATAN Model 682 precision etching and coating system (PECS), using argon, for 4 h, with the current of 350 μA, the accelerating voltage of 6 keV, and the rotation rate of 10 rpm [12].

Compared to polishing, this method allows eliminating the surface layer more completely but in the case of irregular surfaces such as the interface chromia/Inconel®625, the ion beam etching does not avoid attacking the substrate asperities. **Figure 8(a)** presents the surface condition of the alloy after the complete removing of the chromia layer, and **Figure 8(b)** shows different kinetics performed, *i.e.*:

1) That obtained by a simple 10 hours-heating (360,000 s) at 1223 K (purple curve).

2) That obtained after a 10-hours heating at 1223 K, cooling, and re-heating 5 hours more at the same temperature: such as in **Figure 7(b)** this curve (red) is in the perfect continuity of the purple curve, confirming the good reproducibility of the kinetics and also that the cycle {cooling/re-heating} does not affect the kinetics.

3) That obtained after a 10-hours heating at 1223 K, cooling, removing partially the chromia layer by ion-beam etching (the substrate was not attacked at all, but it remains a very thin layer of chromia linked to the alloy) and re-heating at 1223 K 5 hours more: this curve (green) is quasi-perfectly superimposed on the red one, which confirms that the partial elimination of the chromia layer does not affects the kinetics, and hence proves that this layer was not the diffusion limiting step.

4) That obtained after a 10-hours heating at 1223 K, cooling, removing entirely the chromia layer by ion-beam etching (the substrate surface condition was that of **Figure 7(a)**) and re-heating at 1223 K 5 hours more: this curve (blue) presents a slight restarting, justifiable as explained in the section before, since the thickness of the diffusion zone inside the alloy was slightly diminished by the attack of the alloy.

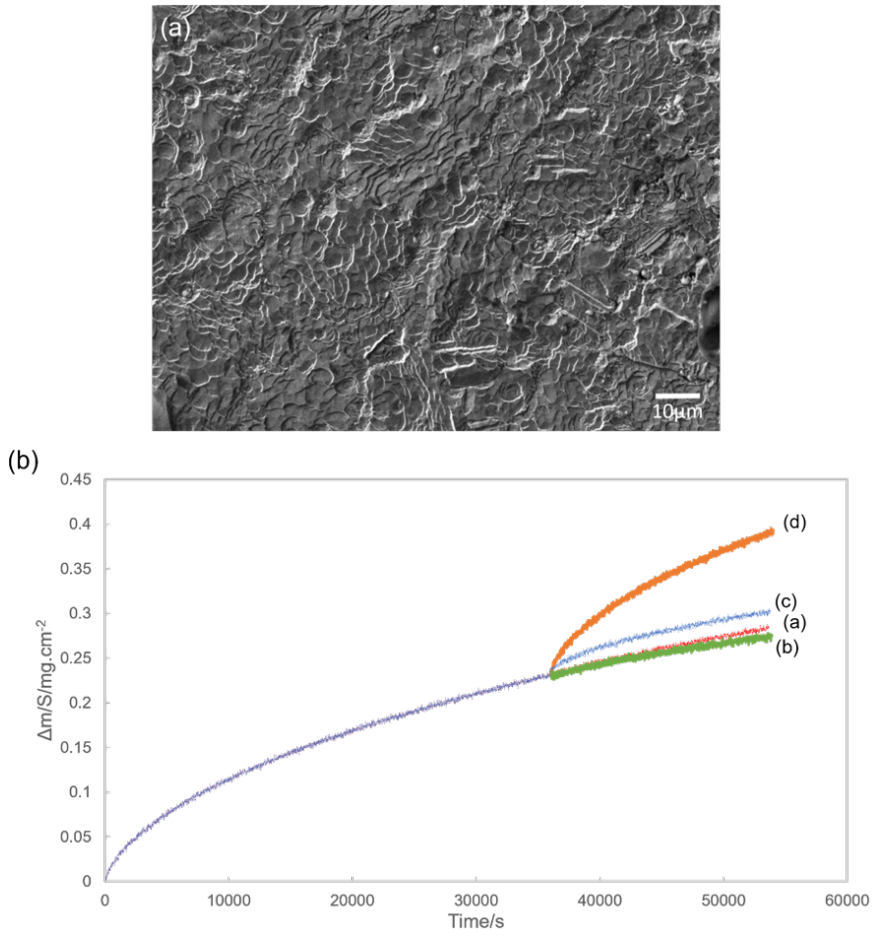

Figure 8. Ion beam etching of the partially oxidized Inconel®625 at 1223 K in CO_2 and re-oxidizing. (a) Aspect of the surface after the complete removal of the chromia layer and (b) the corresponding kinetics: in purple the curve obtained with a 10-hour heating; in red the curve (a) obtained by a direct 15-hour heating; in green the curve (b) obtained with a 10-hour heating, then slightly ion etching the sample, and then re-heating for 5 extra hours; in blue the curve (c) obtained with a 10-hour heating, then completely removing the chromia layer by ion etching, and then re-heating for 5 extra hours; in orange the curve (d) drawn by placing again the beginning of the kinetic at the coordinates (0.22; 360,000) [12].

5) The orange curve added in **Figure 8(b)** represents what might occur if the chromia layer was protective. It is the duplication of the first 5 hours of oxidation, reported at the time of 10 hours and at the mass increase $\Delta m/S = 0.22$, in order to illustrate the restarting that could be observed in the case of a protective chromia layer. The large difference between this (theoretical) curve and the green or blue curves (obtained experimentally) confirms the non-protective nature of the chromia layer.

3.2.3. Comparison of the Two Removal Methods and Their Advantages

Both methods presented here for eliminating the surface oxide formed by the oxidation of chromia-forming alloys are rather basic, but they allow to determine without ambiguity whether the chromia surface layer is protective or not. However, these methods have been completely ignored or neglected in previous articles

on the oxidation of chromia-forming alloys.

Polishing is by far the easiest to implement, but it may introduce impurities (polishing residues) likely to disrupt the further TGA. Ion beam etching is a much cleaner method, but it requires the use of more complex equipment.

In fact, polishing appears to be a good first approach method for controlling the protective character of surface oxide layers formed on chromium alloys, but ion beam etching should be preferred for further study.

Experimentally, in both cases, it must be noticed that these methods require a lot of back and forth between observations of the surface and removal of the oxide layer in order to control the level of removing progressively obtained and, particularly in order to avoid any significant attack of the substrates.

3.3. Cases Where the Question of the Protective Nature of Chromia Could Be Raised

Numerous studies have been devoted to the growth of chromia layers, particularly on Ni-Cr alloys with more than 20% Cr, often containing other metals such as molybdenum, following parabolic kinetics [15]-[20]. Even if the nature of the gas and the temperature changes, the chromia layer formed is always considered as protecting the underlying alloy (with sometimes co-oxidation processes forming simultaneously other oxide such as NiO or TiO_2 [10] that perturbs the kinetics). Clearly, the understanding of the oxidation resistance in such alloys have been focused on the diffusion mechanisms occurring inside the oxide layer [8] [21].

The same applies to the oxidation of pure chromium, which is the first case studied below.

3.3.1. Case of the Oxidation of Pure Chromium

The oxidation of pure chromium has been the subject of much study and controversy, and for a long time [22] [23]. It is still being studied in more recent articles [24] [25]. These articles are mainly devoted to the characterization of the chromia layer, the kinetics being parabolic, at least above 1173 K. Such as in the system Inconel®625/CO_2, the oxide layer always presents many buckling, but, in the case of pure chromium, there are some significant differences with scaled areas and above all there is no porosity inside the metal substrate.

Here, not any chromium gradient can exist in the substrate, and the parabolic kinetics were obviously due to the limiting step of diffusion inside the chromia layer.

Consequently, the removal of this layer would necessarily lead to the restarting of the kinetics, in conditions similar to the orange curve placed in **Figure 8** above. Nevertheless, it would be interesting to carry out an oxide layer removal test to verify this assertion.

At this point, it is also interesting to note that the activation energy for the oxidation of pure chromium is around 250 - 290 kJ·mol^{-1} [24] given that the limiting step is diffusion through the chromium layer, whereas it is significantly higher in the Inconel®625/CO_2 system (310 ± 18 kJ·mol^{-1} [12]) where the limiting step is

chromium diffusion within the alloy. Despite the need for caution about the signification of the apparent energies of activation, this difference might be due to the fact that the limiting step is not the same in the two cases.

3.3.2. Case of the Oxidation of the Ni-Cr Alloys

Since the 1970s, many authors have published about the formation of the oxide layers on Ni-Cr alloys by oxidation in various atmospheres, but the results are not always consistent, either in terms of kinetics or even the nature of the oxide obtained. The results are significantly different depending on the composition of the alloy [17], the temperature, the atmospheres [18], the duration of treatment and even the grain size of the alloy [19]. For example, **Figure 9(a)** illustrates the accelerating role of water on the oxidation rate of a Ni-20Cr type alloy at 1323 K.

Nevertheless, the main features of the oxidation observed in the present work (irregular and dense chromia layer, porosity inside the alloy and chromium-depleted zone of the alloy close the interface with chromia) are more often observed (see **Figure 9(b)**) despite of frequent significant differences, in particular, the spallation occurring at the surface of chromia during oxidation in oxygen or air [26]. Also, the presences of NiO, $NiCr_2O_4$ [19] and of titanium [10] are sometimes reported in the oxide layer for long-term treatments or transient oxidations at high temperatures and for low oxygen pressures, where the chromia is more or less porous [7] [27].

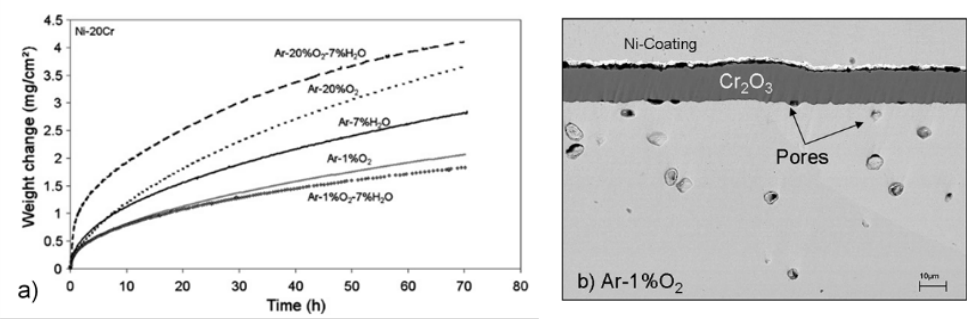

Figure 9. Isothermal oxidation of a Ni-20Cr type alloy at 1323 K: (a) kinetics in various atmospheres; (b) cross section after 72 hours in Ar-1% O_2 [19].

Kinetics are generally parabolic and influenced by oxygen pressure, but it was often mentioned that the rate was faster at the beginning of the reaction and susceptible to be fitted with the complete law for parabolic oxidation for times of several hundreds of hours [25]. In fact, the reaction mechanism identified in most articles appears not to be unique when the oxidation time is prolonged and, moreover, the role of the diffusion of chromium in the alloy from the core to the surface has rarely been considered [27]. It is obvious that this last point, a major one in the case of the oxidation of Inconel®625 in CO_2, has not been sufficiently considered and that not all the consequences have been drawn about the slow diffusion of chromium in Ni-Cr alloys.

It is also rather surprising that the simple experiment to remove the oxide layer,

described above, was never mentioned in the articles cited, or in any other. This could have provided interesting and useful additional information on the reaction mechanism, particularly in cases where Cr depletion within the oxidized alloy has been identified.

In these conditions, among the very many articles devoted to the oxidation of Ni-Cr alloys, and more generally of chromia-forming alloys, and especially at the beginning of the reactions, *i.e.* at least as long as the oxide layer remains composed exclusively of chromia and is less than 2 - 3 μm thick (values observed in the present study on Inconel®625), it is possible that, in a certain number of cases, the decreasing kinetics observed are not due to the protection of the chromia layer, contrary to what is currently accepted.

Moreover, the effect of the pressure must be carefully considered. Indeed, if the limiting step is located inside the alloy, there is not any influence of the gas pressure on the reaction rate, such as observed for the system Inconel®625/CO_2. This lack of pressure influence is also mentioned in the case of other chromia-forming alloys [27] and these cases that might be re-examined as a matter of priority, as they are the closest to the Inconel situation.

4. Conclusions

The present work follows on from a previous one devoted to the detailed mechanism of dry corrosion of Inconel®625 in CO_2 [12]; it demonstrates unambiguously that the chromia layer formed by oxidation is not protective in this case. This result contradicts a general opinion that has always been accepted, until now, for other chromia-forming alloys. Here, Inconel®625 is also effectively protected against oxidation, under the conditions of this study, but this protection is achieved through the change in composition of the underlying alloy, not through the chromia layer.

This conclusion could have substantial industrial consequences because it means that, even if the chromia layer disappears from the surface of industrial pieces (for instance by rubbing), these pieces may continue to be protected against oxidation, contrary to what was considered before. Hence this could revive the production of chromia-forming alloys for certain applications.

On top of that, the method used for demonstrating that the chromia layer is not protective is a very simple one and that can be very easily implemented: it consists in simply removing from the alloy surface the chromia formed by oxidation, which can be achieved by polishing or by ion etching.

This experimental method could have been used in many other studies of chromia-forming alloys, but was not. Consequently, it is possible that, when tested on other chromium alloys, this method will also demonstrate that the chromia layer observed is not protective in certain cases, contrary to what has been admitted previously in many articles, and in particular when there is no influence of the gas pressure, as seen in the previous paragraph.

It is desirable that the present article encourage the relaunch of studies on the

oxidation of other chromia-forming alloys, which are among the most frequently used in industry, in order to confirm—or not—the protective character of the chromia layers, by using the method developed here and that could have been implemented for long in many cases.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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