Influence of the microstructure fineness on the high temperature oxidation during heating and on the oxide spallation during cooling for carbides-strengthened cast superalloys

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ABSTRACT

The heating parts and cooling parts of thermogravimetry curves obtained for nickel-based and cobalt-based superalloys, solidified either slowly or more rapidly, were studied in order to look for a possible influence of the microstructure fineness on the first stage of oxidation (at heating) and the resistance of the external oxide isothermally formed against spallation (at cooling). Compared with a fine microstructure, a coarse microstructure obtained by a slower solidification tends to enhance oxidation at heating, with a lower temperature of oxidation start and finally a higher mass gain at the end of heating. A coarse microstructure also favours spallation, which may be due to the greater quantity of oxide to which the coarse microstructure led because of a slightly faster isothermal oxidation compared to the fine microstructure. A high temperature of isothermal oxidation, and the presence of other very oxidable elements such as tantalum, also tend to enhance spallation at cooling by either increasing the quantity of oxide present before cooling, or by reducing the adherence of external chromia on the alloy surface.   © 2009 Trade Science Inc. - INDIA

INTRODUCTION

The microstructure of alloys resulting from classical foundry practice depends, not only on their chemical composition, but also on the solidification conditions[1]. For example the cooling rate at solidification governs the grain size: the faster the cooling, the finer the microstructure. This can have great consequences on the behaviour of the alloys, notably on their mechanical properties.

But the fineness of the microstructure of an alloy or superalloy obtained by solidification, may also influence its behaviour in oxidation at high temperature[2], as already seen in previous studies[3-5] for the isothermal oxidation kinetic. The purpose of this work is to study if the fineness may also influence other characteristics of the behaviour of alloys in high temperature oxidation, more precisely the transient oxidation at heating and the stability, or in contrary the spallation, of the external oxide formed on long time in isothermal conditions, when the oxidized alloy is cooling.

EXPERIMENTAL

Synthesis of the studied alloys and preparation of the samples for the oxidation tests

Four superalloys, one Ni-based one and three Co-based ones, were elaborated by High Frequency induction foundry. Per alloy (chemical composition given in TABLE 1), one ingot was slowly solidified (in a sand mould) and one ingot was rapidly solidified (in a metallic mould). All alloys contained, in the grain boundaries, one or two types of carbides (eutectic $Cr_{23}C_6$ and/or TaC) known to be very useful for reinforcing polycrystalline superalloys at high temperatures[6,7]. These microstructures, the coarse ones (characterized by a mean spacing between two secondary dendrite arms $\lambda \cong 50$ μm) and the fine ones ($\lambda \cong 25\mu m$) are illustrated, and the phases described, in the micrographs given in figure 1.

For each alloy, two (Ni1, Co1 or Co3) or six (Co2) parallelepipedic ($10 \times 10 \times 2mm^3$) samples were cut for the oxidation tests, one (or three) in the ingot with a coarse microstructure, and one (or three) in the ingot with a fine microstructure. These samples were polished with 1200-grit papers, with smoothing of their edges.

The thermogravimetry tests performed

The oxidation tests were performed during 100 hours at 1000^0C (all alloys), 1100 and 1200^0C (only the Co2 alloy for these two higher temperatures), using a Setaram TGA92 apparatus and under a flow of industrial air ($80\% N_2$-$20\% O_2$) of about 1.5L min^{-1}. The heating and the cooling before and after the 100h-isothermal dwell, were done at +20K min^{-1} and -10K min^{-1} respectively. After testing, the oxidized samples were covered by a gold layer by cathodic plasma pulverisation. This allowed the external surface to become electrically conductive, for the growth of a thick electrolytic nickel coating deposited for mechanically protecting the remaining parts of the external oxide scales formed. Thereafter samples were cut, embedded in resin, polished and examined using a Scanning Electron Microscope (SEM, Philips XL30).

Analysis of the start of oxidation at heating

The thermogravimetry curves were drawn by plotting the mass gain versus time. The equation of the
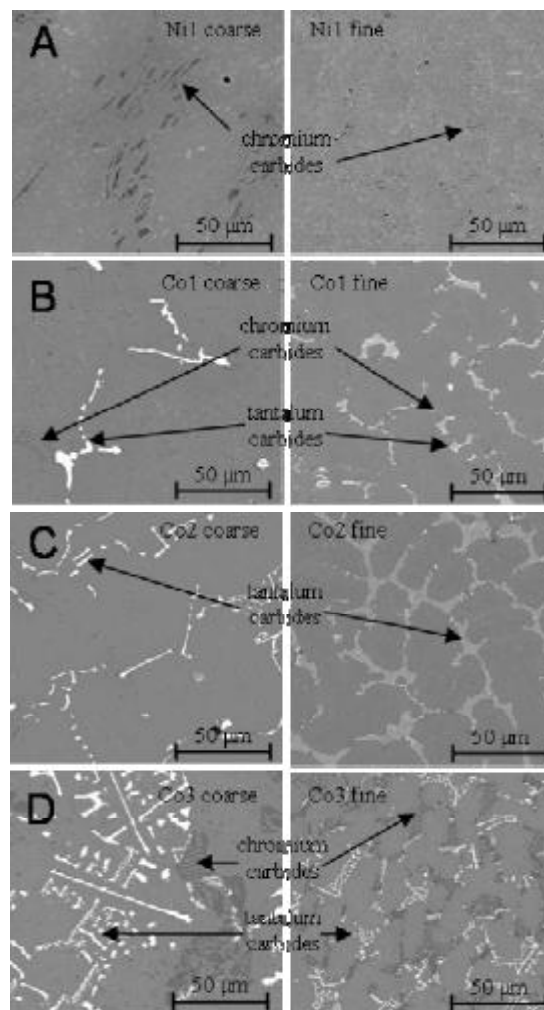

Figure 1: Microstructures of the four alloys (Ni1: A, Co1: B, Co2: C, Co3: D) with a coarse (left) or a fine (right) microstructure (Scanning Electrons Microscope in Back Scattered Electrons mode)

TABLE 1: Chemical compositions of the studied cast superalloys

Weight %	Ni	Co	Cr	C	W	Ta	Fe
Ni1	bal.	/	30	0.7	7.5	0	7.5
Co1	9	bal.	30	0.4	6	3	/
Co2	9	bal.	30	0.4	/	6	/
Co3	9	bal.	30	1.0	/	6	/

linear increase in mass appearing in the high temperature part of the heating curve was determined, and this equation was used for correcting the measured values from the Archimedes' thrust which induced an apparent mass gain not due to oxidation but due to the buoyancy variation of air when temperature increased[8]. The temperature of oxidation start during the heating was then revealed when the mass gain accelerated and quitted this linearity. The total mass gain during heating was also deduced from the curves corrected from the

Archimedes' thrust, as well as the total isothermal mass gain during the 100 hours of isothermal dwell.

Analysis of the spallation of the external oxide at cooling

On the cooling part of the curve the mass evolution is almost horizontal, although one can see in some cases
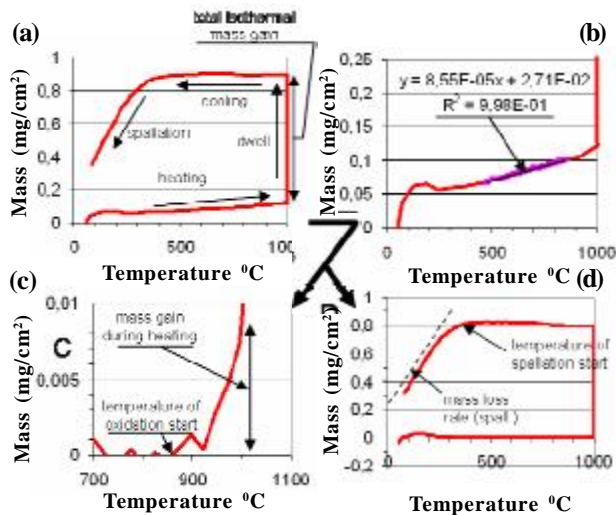

Figure 2: Illustration of the successive steps allowing the characterization of both the transient oxidation at heating and the spallation at cooling: mass gain plotted versus T (a), determination of the equation of the linear part of the heating curve (b), correction with this equation of the whole curve and analysis of the transient oxidation (c) and of the spallation (d)

a small bending of oxide detached from the bulk under the compressive stress progressively developed during cooling because of the differences of thermal expansion or contraction coefficient between the oxides ($\alpha_{oxide} \approx 10 \times 10^{-6}$ K^{-1}) and the alloys ($\alpha_{alloy} \approx 20 \times 10^{-6}$ K^{-1}) [9,10]. When temperature has lost several hundreds degrees, the mass begins to decrease, either with a low rate (it is then simply related to the increase in Archimedes' thrust which enhances the apparent mass loss when the term (T-293K)/T (T = temperature of the sample) increases more and more rapidly, or significantly faster (e.g. much higher than about -0.5μg/cm²/K in the [25^{0}C; 500^{0}C] range) with a more or less irregular part of cooling curve, when spallation really takes place. When spallation obviously occurred, the temperature at which the phenomenon begins and the average rate of mass loss due to spallation are assessed on the cooling curve.

All these determinations are explained and illustrated in figure 2.

RESULTS AND DISCUSSION

Oxidation during heating

Although the heating rate was the same for all alloys and for the two microstructure fineness there are generally differences about the temperatures at which
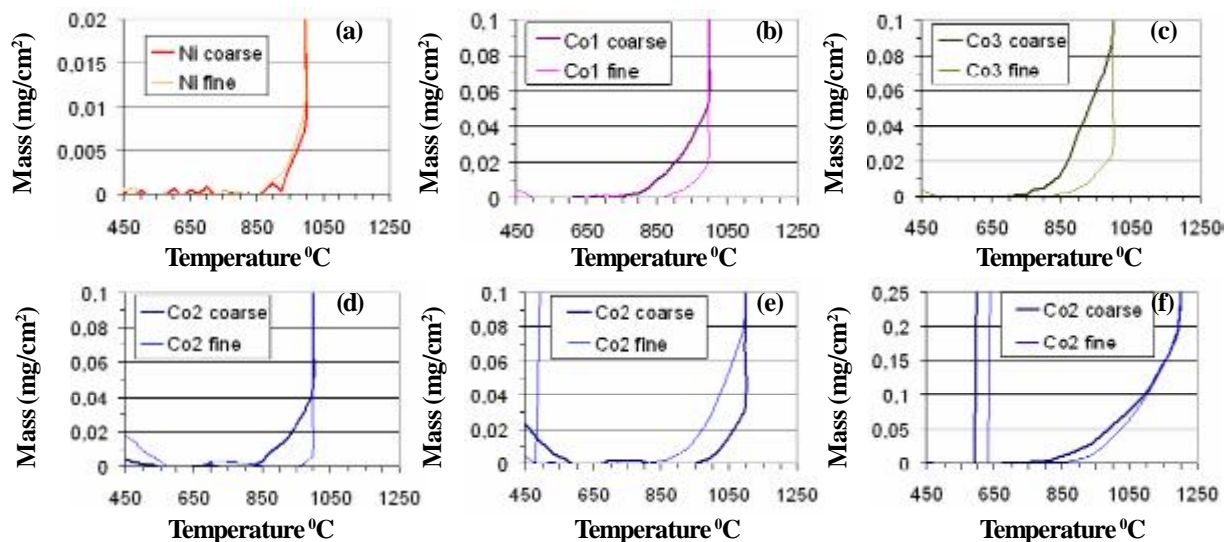

Figure 3: Start of oxidation at heating and the corresponding mass gains curves for the coarse and the fine microstructures of a same alloy in each graph; until 1000^{0}C: Ni1(a), Co1 (b) and Co3 (c); Co2 until 1000^{0}C (d), 1100^{0}C (e) or 1200^{0}C (f)

oxidation obviously started and the total mass gain achieved when the targeted temperature was reached. It is especially more obvious concerning the consequences of the differences of fineness for a same alloy, as it can be seen in figure 3 in which the mass gains near the end of heating are plotted for both the coarse microstructure and the fine one in the same graph for each alloy: if the values of temperature of oxidation start and total mass gain during heating until 1000°C are seemingly equal for the Ni-based superalloys (Ni1) there are differences for the three Co-based superalloys since oxidation started earlier (i.e. at lower temperature), and the total mass gain finally obtained at the end of heating was greater, for their coarse versions than for their fine versions. In contrast this order is inversed for Co2 when it was oxidized until 1100°C while there is no significant difference between the two fineness for this alloy when it was oxidized until 1200°C.

All values are graphically presented together in figure 4. In the histogram A, one can see that the temperatures of oxidation start at heating are almost the same for the two fineness of microstructure in the case of the superalloys Ni1 and Co2. For the latter one the average of the three values measured for the three targeted temperatures 1000, 1100 and 1200°C was considered, since the isothermal oxidation must have no influence of course. In contrast the temperature of oxidation start at heating seems being several tens lower for the coarse Co1 and Co3 than for their fine corresponding versions. The histogram B shows that the heating until 1000°C induced higher mass gains by oxidation for the coarse microstructures, than for the fine microstructures, for all the four superalloys. The order is inversed at higher targeted temperature for the Co2 superalloy (the heating mass gain of which logically increases with the targeted temperature for the two microstructure fineness).

Oxide spallation during cooling

The cooling parts of the thermogravimetric curves display different features, depending on both the alloy and the microstructure fineness, as it can be seen in figure 5. In addition, the temperature at which the 100 hours-isothermal oxidation was realized, seems also having an effect, as seen in the three pairs of curves corresponding to the Co2 superalloy. For the Ni1 and
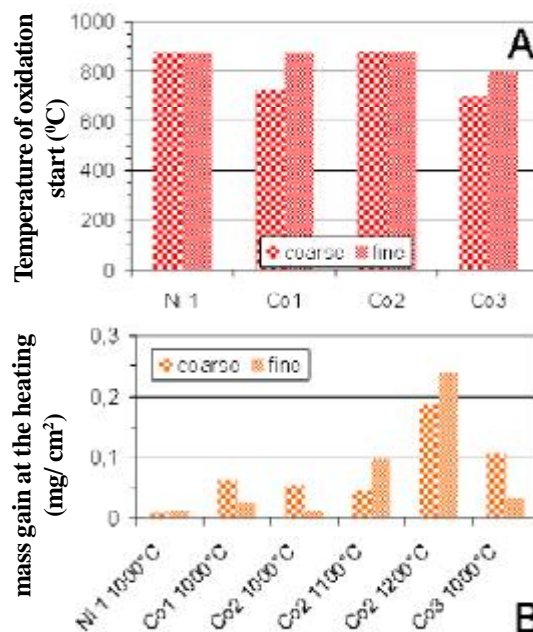

Figure 4: Histograms representing, for all alloys and for the two microstructure fineness, the results of analysis of the heating parts of the thermogravimetric curves: the temperature at which oxidation started with a measurable mass gain (A) and the total mass gain due to oxidation achieved until reaching the targeted isothermal temperature (B)

Co3 superalloys, the cooling thermogravimetric curves are almost the same for the two types of microstructure. At 1000°C too, in contrast there are differences between the two microstructure fineness for the Co1 superalloy and the Co2 one, since, in their cases, spallation occurred for the coarse versions and not for the fine versions (for which there was also a mass gain jump due to oxide bending in the case of Co1). The cooling curves of Co2 after a 100h-oxidation at 1100°C are affected by a jump due to oxide bending (coarse microstructure) and a severe spallation (fine microstructure) which moreover began early, i.e. at a temperature especially high (about 800°C). After oxidation at 1200°C, spallation occurred very early too, with especially rapid mass losses, whatever the microstructure fineness.

All these results are summarized in the two histograms displayed in figure 6. One can see that spallation systematically occurred for the superalloys with a coarse microstructure, at all temperature, while only two alloys (Ni1 and Co1) with a fine microstructure were affected by this phenomenon after isothermal oxidation
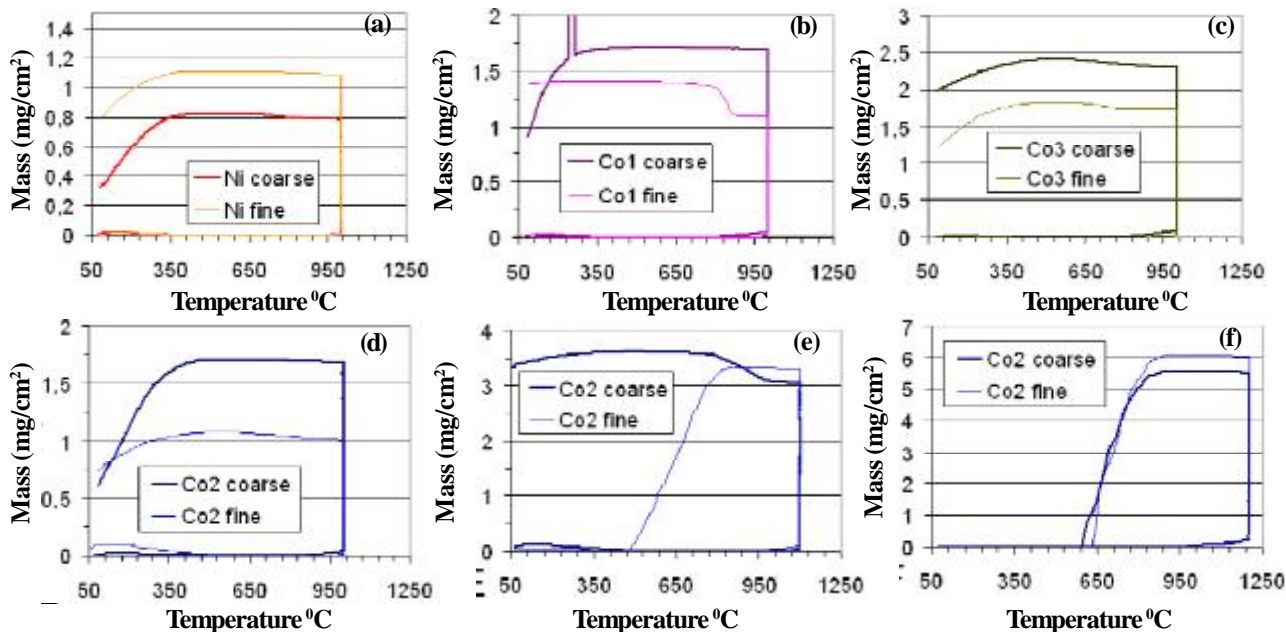
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Figure 5: Occurrence of spallation or not in the mass gain curves at cooling for the coarse and the fine microstructures of a same alloy in each graph; until 1000⁰C: Ni1(a), Co1 (b) and Co3 (c); Co2 until 1000⁰C (d), 1100⁰C (e) or 1200⁰C (f)
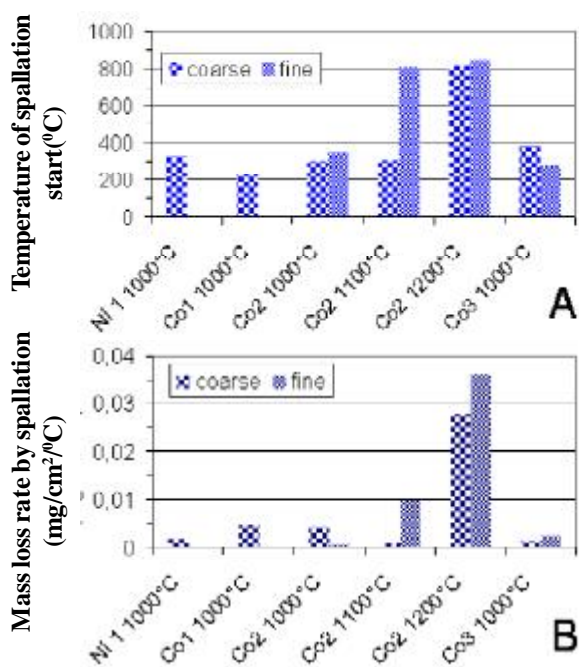

Figure 6: Histograms representing, for all alloys and the two microstructure fineness, the results of analysis of the cooling parts of the thermogravimetric curves: the temperature at which spallation started (if it occurred) (A) and the corresponding mass loss rates (B)

at 1000⁰C. In contrast, oxidation during 100 hours at higher temperatures than 1000⁰C led to spallation for all the alloys, whatever the fineness of the microstructure. Inversely, there is no systematic dependence of the temperature at which spallation began on the microstructure fineness (figure 6, A). This is also true for the mass loss rate due to oxide spallation (figure 6, B).

General commentaries

Differences were thus found about both the oxidation beginning occurring during the heating and the loss of oxide by spallation during the cooling, when the nature of the concerned alloy changed and when its microstructure was more or less fine or coarse. In the case of the transient oxidation starting when the temperature raised upto the isothermal temperature, it seemed that a coarse microstructure favoured an early oxidation (i.e. when temperature was still not very high). This could be explained by the fact that coarse intergranular carbides, which contain high concentrations of very oxidable elements (Cr but also Ta in some cases), are more easily exposed to oxidation. But one must be careful since the three tests performed with the Co2 superalloy (for three different targeted temperatures) led to different hierarchies of temperature of oxidation start between the two microstructure fineness. It is then possible that there was a problem of reproducibility which must be understand before concluding. Concerning the total mass gain achieved at the end of heating, the differences between the two microstructures fine-
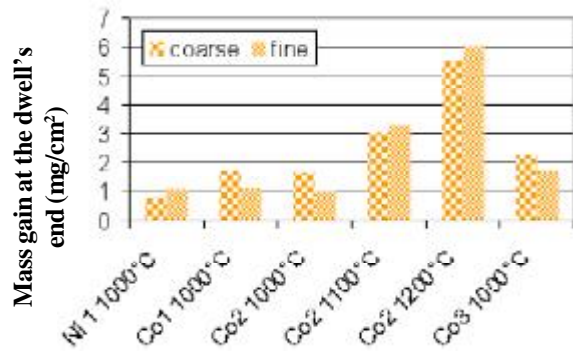
Figure 7: Histogram representing, for all alloys and the two microstructure fineness, the mass gains obtained by transient oxidation and isothermal oxidation before cooling
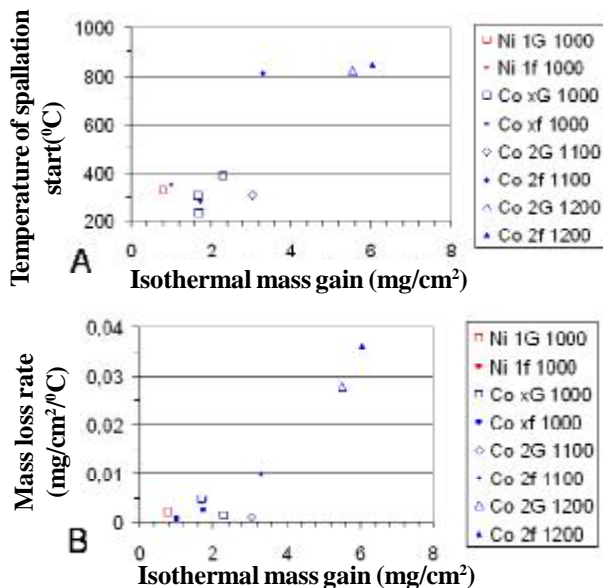

Figure 8: The two studied spallation characteristics plotted versus the total mass gain due to oxidation before cooling

Figure 9: SEM micrographs of the oxidized surfaces of the Ni1 superalloy oxidized at 1000⁰C and the Co2 superalloy oxidized at the same temperature, both with the fine microstructure (taken in BSE mode)

ness could be more related to the temperature of oxidation start than to this microstructure fineness since the higher the temperature start the lower the mass gain at the end of heating.

Concerning the spallation phenomenon, for cooling from 1000⁰C it was more often the coarse microstructure which led to spallation than the fine one. This is inversed for 1100⁰C with the Co2 superalloy, while spallation occurred for the two microstructure fineness for 1200⁰C. Therefore one can think that spallation may be more easily related to the total mass or thickness of oxide obtained at the end of the isothermal oxidation. It is the reason why the different total {transient + isothermal} mass gains, measured on the whole curves
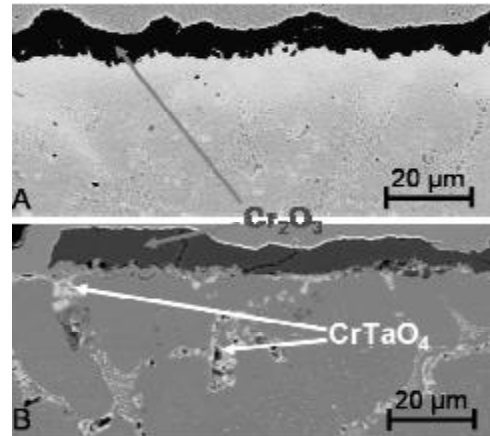
presented in figure 5, and summarized in a histogram in figure 7, were taken into consideration. Plotting the two studied characteristics of spallation versus the total mass gain achieved just after isothermal oxidation show that spallation is generally favoured by a great quantity of oxide previously formed (figure 8).

Another parameter which can be important for the oxide spallation is also the type(s) of oxide(s) formed. If the greatest part of external oxide was chromia for all alloys, the Ta-containing alloys can be concerned by the appearance of an interfacial and more or less regular oxide of both chromium and tantalum (figure 9). As previously encountered for nickel-based alloys[11], it is possible that the formation of an inner layer of $CrTaO_4$ oxide could threaten the adherence of chromia on the superalloy surface. This can explain why the Ta–richest superalloys (Co2 and Co3, with 6wt.%Ta) encountered spallation, even for the fine microstructure.

CONCLUSIONS

The characteristics of the oxidation start at heating as well as the spallation of the external oxide form at cooling can vary with the microstructure fineness of cast superalloys resulting from the rate of their solidification. This study tends to show that the coarse microstructure should favour an early oxidation, and as a consequence, more oxide formed during the heating. But confirmation may be needed because of a fair reproducibility

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which could be due to another parameter: maybe the other principal texture characteristic which is dendritic orientation. Results were clearer for oxide spallation since a high quantity of oxide, which depends also on the microstructure fineness for given oxidation temperature and duration, obviously promotes more spallation. The role of tantalum, favourable to spallation, was also found again whatever the microstructure fineness.

REFERENCES

[1] W.Kurz, D.J.Fisher; 'Fundamentals of Solidification', Trans Tech Publications, **(1989)**.

[2] P.Kofstad; 'High Temperature Corrosion', Elsevier Applied Science, London, **(1988)**.

[3] P.Berthod, S.Raude, A.S.Renck, C.Rapin, R.Podor, P.Steinmetz; Materials Science Forum, **461-464**, 1173 **(2004)**.

[4] P.Berthod, S.Raude, A.Chiaravalle, A.S.Renck, C.Rapin, R.Podor; La Revue de Métallurgie-CIT/ Science et Génie des Matériaux, **12**, 1031 **(2004)**.

[5] P.Berthod, S.Raude, A.Chiaravalle; Annales de Chimie-Science des Materiaux, **31(2)**, 237 **(2006)**.

[6] E.F.Bradley; 'Superalloys: A Technical Guide', ASM International, Metals Park **(1988)**.

[7] C.T.Sims, W.C.Hagel; 'The superalloys', John Wiley and Sons, New York, **(1972)**.

[8] P.Berthod, L.Aranda, P.Lemoine; Materials Science: An Indian Journal, **5(1)**, **(2009)**.

[9] P.Shaffer; 'High-Temperature Materials N°1', Plenum Press, New York, **(1964)**.

[10] G.V.Samsonov; 'High-Temperature Materials N°2', Plenum Press, New York, **(1964)**.

[11] P.Berthod, L.Aranda, C.Vebert; Materials Science: An Indian Journal, **5(1)**, **(2009)**.