Oxide spallation during cooling from high temperatures affecting carbides-containing nickel-based alloys. Part 1: Case of ternary Ni-Cr-C alloys with various carbides fractions

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ABSTRACT

When an alloy preliminarily exposed to high temperature in an oxidizing atmosphere is cooled, its external oxide protective scale can be more or less lost, depending on the thickness of the oxide and on the characteristics of the alloy. This spallation phenomenon was here studied for Ni-30wt.%Cr-based alloys containing various amounts in carbon, by exploiting the mass variations recorded in the cooling parts of thermogravimetry curves. It was seen that chromia spallation tends to be more severe, in terms of cooling before start, mass loss rate and final fraction of oxide loss, when the temperature of previous isothermal oxidation is higher and when the carbides fraction in the alloy's microstructure is lower. This highlights probable effects of the quantity of oxide formed before cooling and of the thermal contraction of the alloy. © 2009 Trade Science Inc. - INDIA

INTRODUCTION

After exposure to oxidizing atmospheres at high temperature, heat-resistant alloys are covered by an oxide scale protecting them from fast oxidation. This protection supposes that the scale is continuous, adherent enough, and made of a stoichiometric oxide (such as Cr_2O_3 and Al_2O_3) to limit diffusion of ions involved in the oxidation phenomenon[1,2]. Unfortunately, temperature usually does not remain constant on long times in service, and then the protective scale is partially (and sometimes even totally) lost because of the significant differences of thermal expansion or contraction existing between the bulk alloy and the external oxide. During temperature cycling, because of this spallation, the repetition of new and rapid oxidation of the denuded alloy accelerates the impoverishment in chromium or aluminium in the sub-cortical alloy area which can then rapidly loose its initial chromia-forming or alumina-forming behaviour. Depending on the thermal expansion coefficients of both the oxide and the bulk alloy, but also on the adherence of the scale on the alloy substrate, the importance of the external oxide loss, in terms of mass loss rate during cooling or of final denuded surface fraction, can be very different.

In this work, the phenomenon of loss of external oxide by spallation is studied in the case of simple nickel-based alloys containing various fractions in chromium

carbides, then for various thermal expansion behaviours of the bulk and various densities of interdendritic carbides emerging on surface.

EXPERIMENTAL

The studied alloys

The alloys which were under consideration here are all based on nickel, added with the same content in chromium (high enough for allowing a chromia-forming behaviour for the alloys). There are one binary Ni-30Cr and six ternary Ni-30Cr-xC (with x equal to 0.2, 0.4, 0.8, 1.2, 1.6 and 2.0) alloys, all contents being expressed in weight percent. These alloys were synthesized by high frequency induction casting (300kHz, CELES furnace) in inert atmosphere (pure argon, 300mbars). In each case, fusion of pure elements (purity more than 99.9wt.%, average mass of each ingot: 100g) and solidification of the obtained liquid alloy, were both realized in the water-cooled metallic crucible of the furnace.

The thermogravimetry tests were performed at 1000, 1100 and 1200^{0}C using a Setaram TGA 92 thermo-balance, following a thermal cycle constituted by a heating at 20 K min^{-1}, a dwell at the targeted temperature during 50 hours and a cooling at -5 K min^{-1}. Results (varying mass divided by sample area) were plotted versus temperature. The cooling parts of these curves were especially examined, notably in terms of temperature of mass loss beginning, mass loss rate and fraction of oxide remaining on surface.

After electro-deposition of a reinforcing outer nickel layer to prevent any additional loss of oxide during the following operations, cutting, embedding in a {resin + hardener} mixture, and polishing up to mirror state, the oxidized samples were examined with a Scanning Electrons Microscope (SEM, Philips XL30) in order to observe the oxidized surfaces.

RESULTS AND DISCUSSION

Thermogravimetry results recorded during cooling

The whole mass gain curves obtained are globally all of the type described in the synthetic curve drawn in figure 1, when plotted as a function of temperature. They

are presented in figures 2-4 for a temperature of isothermal stage equal to respectively 1000^{0}C, 1100^{0}C and 1200^{0}C. They include successively:
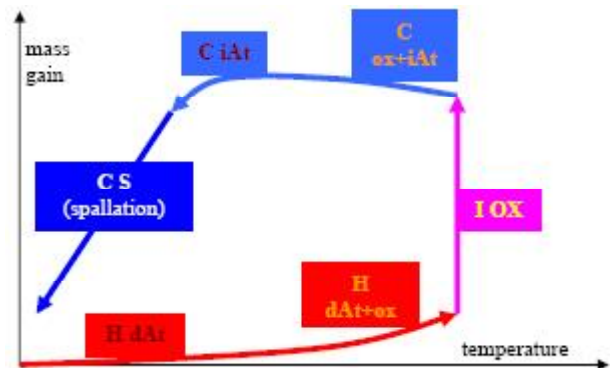

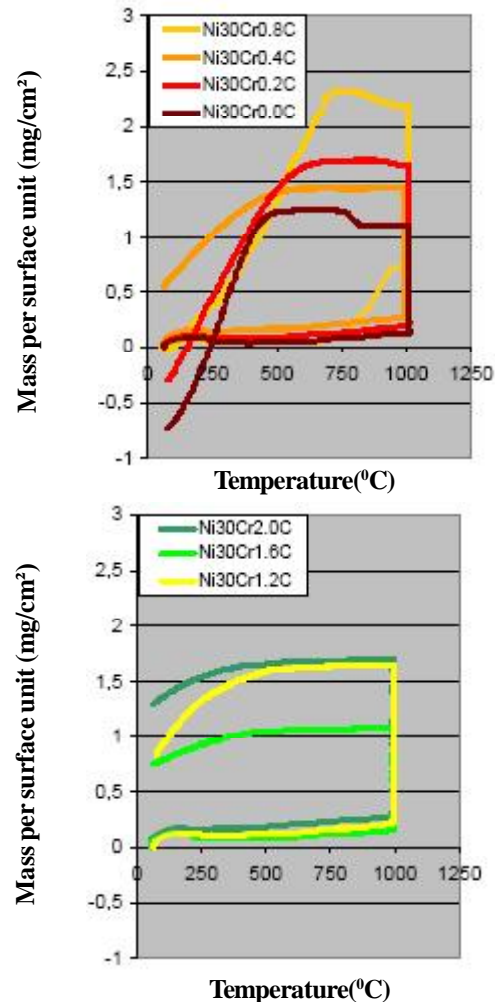**Figure 1: Typical variations of the measured sample mass when plotted versus temperature instead of time**

Figure 2: Mass gain plotted versus temperature for the low C alloys (left hand)and for the high C alloys (right hand) for Tdwell = 1000°C
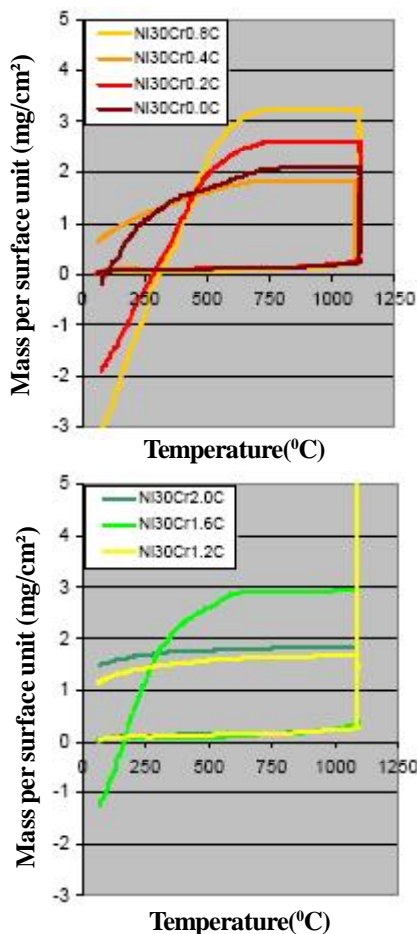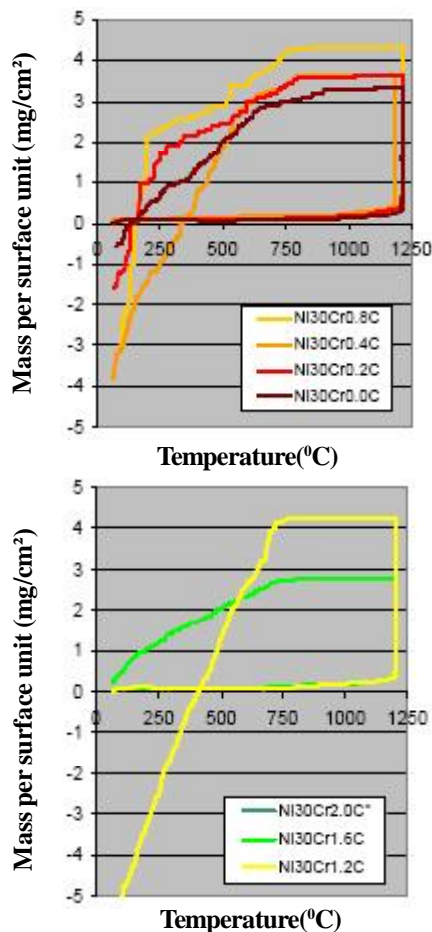
Figure 3: Mass gain plotted versus temperature for the low C alloys (left hand) and for the high C alloys (right hand) for Tdwell =1100°C

Thermogravimetric results are not available for the Ni30Cr2.0C alloy oxidized at 1200°C
Figure 4: Mass gain plotted versus temperature for the low C alloys (left hand) and for the high C alloys (right hand) for Tdwell =1200°C

o a first heating part with a mass gain only due to the decrease in Archimede thrust (designed by "H dAt" in figure 1), followed by a second heating part in which oxidation begins to induce a real mass gain ("H dAt+ox"),

o an isothermal part ("I OX") with a mass gain which generally obeys the parabolic Wagner's law[3] (but which cannot be evidenced here in this type of representation),

o a first cooling part in which oxidation goes on and leads to a small mass gain which is more or less compensated by a decrease in mass due to the increase in Archimede's thrust ("C ox+iAt" then "C iAt")

o and finally a more or less fast decrease in mass due to a more or less severe and progressive spallation of the external oxide ("C S").

heating parts were all of the same type while isothermal oxidation led to more or less great mass gain, depending on both temperature (the higher the temperature, the faster the oxidation kinetic) and the alloy (oxidation rate tends to increase when the carbon content increases, notably in the [0 ; 0.8wt.%C] range). The cooling parts are also all of the same type, as is to say composed of a first almost horizontal first part (high temperatures side), followed by a second part characterized by a more or less important slope. Only one curve (Ni30Cr cooling from 1000°C) is different from the others since it presents a jump analogous to what it was previously observed for simple cobalt-based alloys[4], and which is probably due to a local detachment (but without loss) of a part of the external oxide.
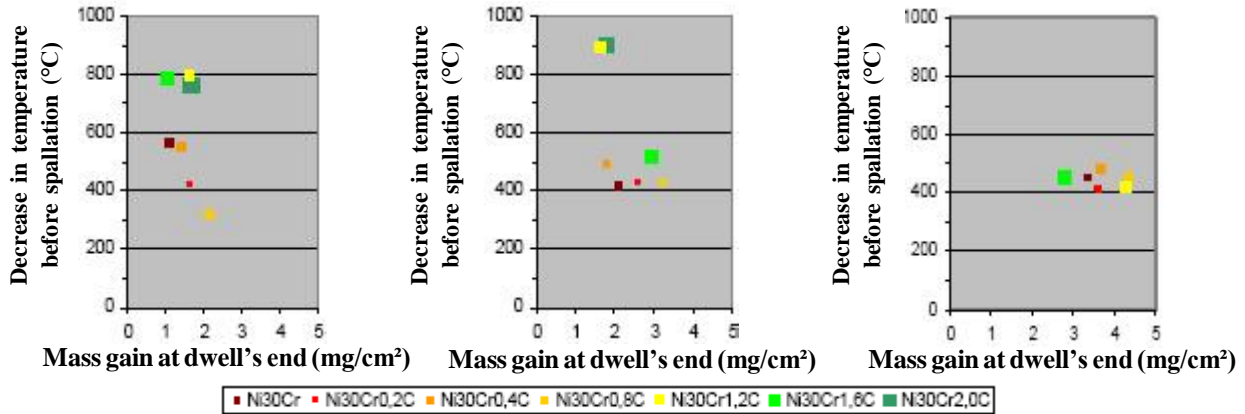
Figure 5: Difference between the dwell's temperature and the temperature at which spallation begins at cooling, plotted versus the mass gain at the end of the isothermal stage: 1000°C (left), 1100°C (middle), 1200°C(right)
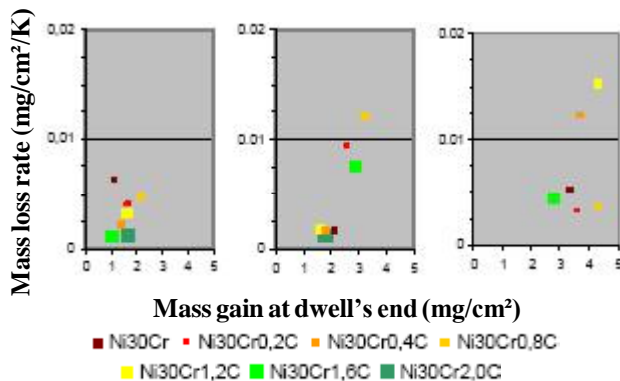

Figure 6: Spallation's rate during cooling, plotted versus the mass gain at the end of the isothermal stage: 1000°C (left), 1100°C (middle), 1200°C(right)

Analysis of the oxide spallation progress

One can suppose that the temperature of spallation beginning and the mass loss rate, for a same cooling rate, may depend on the alloy (notably its thermal contraction behaviour and its possible internal oxidation), on the nature and the total thickness of oxide, and on the temperature from which the cooling started (i.e. the temperature of isothermal stage, on which the mechanical behaviour of the oxide can depend).

From these considerations, three characteristics of oxide spallation were examined, and plotted versus the total mass gain before cooling. Figure 5 displays the decrease in temperature from the dwell's temperature, before start of spallation. Figure 6 shows the average mass loss rate in the temperature range where spallation occurred.

Figure 7 represents the fraction of external oxide lost by spallation during the whole cooling ("Frac Oxid Lost"), calculated by the following formula:

$$\text{FracOxid lost(\%)} = 100 \times \frac{\text{MassReturn Room Temp} - \text{MassGainEndIsothStage}}{\text{Mass Oxid End Isoth Stage}},$$

in which

- "MassReturnRoomTemp" is the mass difference {$m_f - m_i$} between the beginning (initial mass at room temperature before heating, m_i) and the end of the experiment (final mass after return to room temperature, m_f),
- "MassGainEndIsothStage" is the difference of mass of the sample between the beginning of the experiment (m_i) and the end of the isothermal stage; this almost corresponds to the mass of oxygen having joined the sample, m_O, measured by the thermobalance,
- "MassOxidEndIsothStage" is the mass of oxide formed between the beginning of the experiment and the end of the isothermal stage; considering that this oxide is mainly Cr_2O_3[4,5] this quantity is related to the mass gain by the following equation:

$$\text{Mass Oxid End Isoth Stage} = \frac{1}{3} \times \frac{m_O}{M_O} \times M_{Cr_2O_3}$$

- in which M_O and M_{Cr2O3} ($= 2 \times M_{Cr} + 3 \times M_O$) are the molar masses of oxygen and of chromia.

It must be noted that simplifying hypotheses were done to obtain these formula:

S1: The virtual mass gain during heating (due to the decrease in Archimede's thrust) is supposed negli-
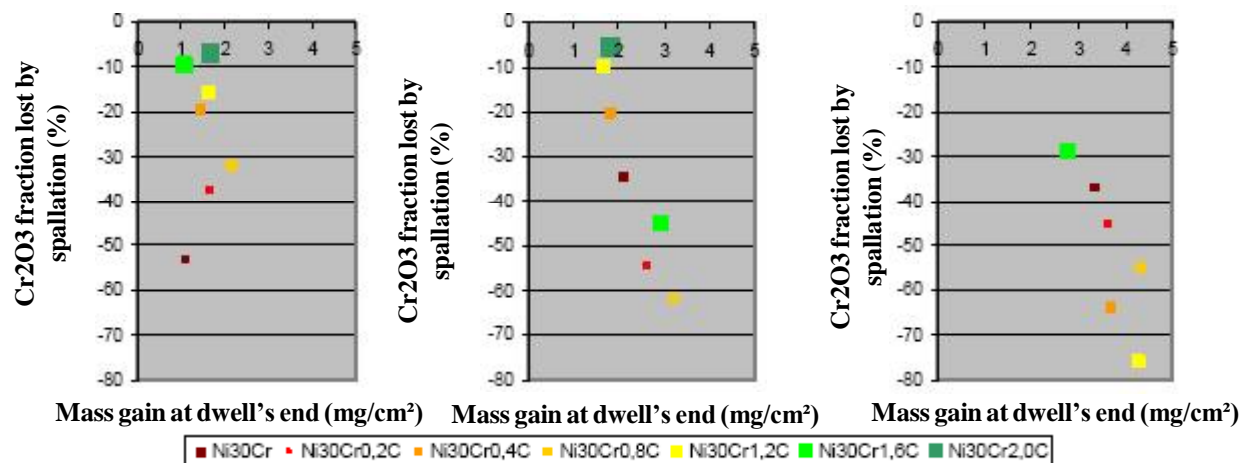
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Figure 7: Fraction of chromia lost at cooling because of spallation, plotted versus the mass gain at the end of the isothermal stage: 1000°C (left), 1100°C (middle), 1200°C (right)
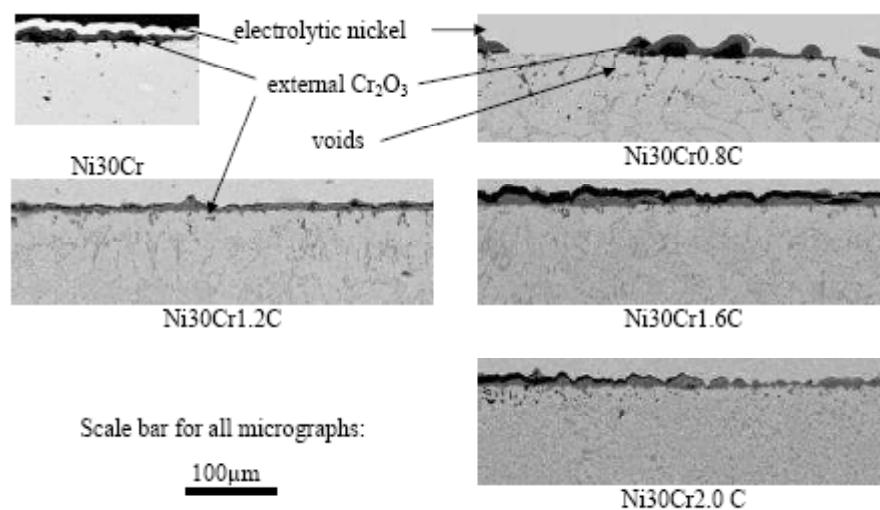

Figure 8: SEM micrographs illustrating the surface state for some of the oxidized samples (1000°C).

gible when compared to the total mass of oxygen having joined the sample before beginning of cooling (oxidation during the last part of heating and the isothermal stage: m_O),

S2: The effect of the increasing Archimede's thrust on the measured sample mass during cooling can also be neglected when compared with the mass loss by spallation,

S3: Chromia (Cr_2O_3) is considered to be the most important oxide in mass, by comparison with NiO which can appear in small quantity at the beginning of oxidation before chromia develops.

S4: Even for the highest stage temperatures (1100 and 1200^{0}C) the mass loss by chromia volatilization due to re-oxidation into volatile CrO_3 oxide can

be neglected.

Spallation seems beginning at a lower temperature (then for a greater decrease in temperature) for the alloys with the highest carbon contents (between 1.2 and 2.0wt.%) than for the other ones (figure 5). Secondly, even if there is no well established order with respect to the carbon content, mass losses seem being faster for the alloys with the lowest carbon contents than for the carbon-richest alloys (figure 6). High mass loss rates are also seemingly favoured by high temperatures of isothermal oxidation (or by great masses of external oxide formed before cooling). This can explain why the fraction of oxide lost noticed after return to room temperature tends to be more important for the low-carbon alloys than for the high-carbon ones, and for high
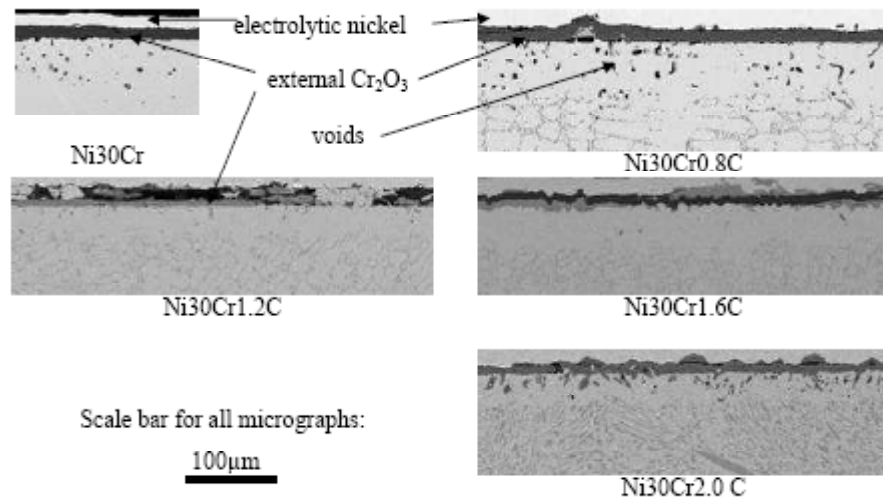
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Figure 9: SEM micrographs illustrating the surface state for some of the oxidized samples (1100°C)
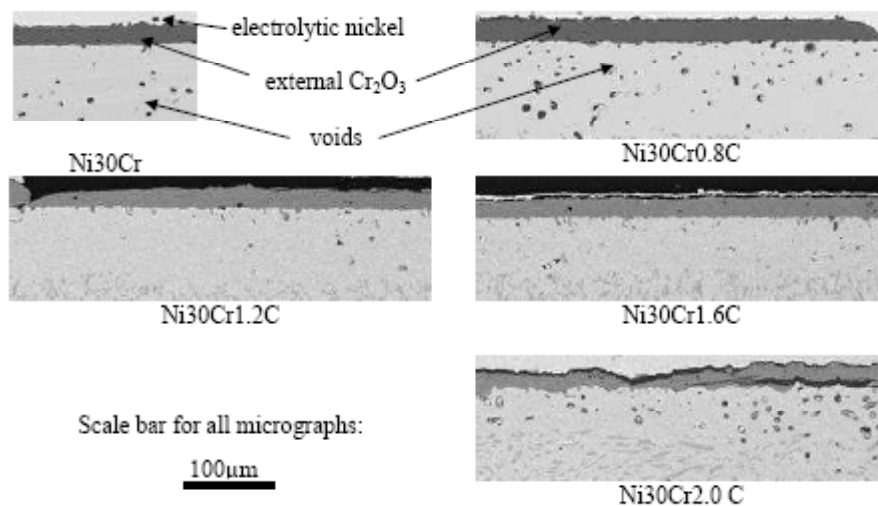

Figure 10: SEM micrographs illustrating the surface state for some of the oxidized samples (1200°C)

temperatures of isothermal oxidation than for low ones (figure 7).

Metallographic cross-sections of the oxidized samples allowed obtaining the SEM micrographs presented in figures 8-10 for respectively 1000⁰C, 1100⁰C and 1200⁰C. One can see that some parts of external oxide were effectively lost since either there are parts of denuded alloy, or the oxide scales have obviously lost their more external part. These micrographs also allow seeing qualitatively that there is a single type of oxide, chromia, and that voids have sometimes appeared in the sub-cortical zone which was affected by oxidation (and which has lost its carbides in the case of the carbon-containing alloys).

General commentaries

It is after a decrease in temperature of several hundreds degrees that scale spallation begins, with a mass loss which was generally almost continuous. The mass loss rate generally tends being faster for the low carbon alloys than for the others with the highest carbon contents, and it is accelerated for the highest dwell's temperature (1200⁰C). There was also a tendency to a pleating of the external oxide scale, as seen on metallographic cross-sections at room temperature, for the alloys with low carbon content, which highlights a compression of the scale during cooling. It is well known that the difference of thermal expansion behaviour between an alloy and its external oxide (coefficient lower

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than the alloy's one) favours spallation. This is true for these alloys based on Ni-30wt.%Cr since there is effectively a significant difference of thermal expansion coefficient between the two: around 18×10^{-6} K^{-1} (with a tendency to lower values when carbides are more present)[7] for the alloys and less than 10×10^{-6} K^{-1} for chromia[8]. This acted here too, with an easier spallation of oxide for the low-carbon alloys for which the difference of thermal contraction between alloy and oxide was a few greater than for the high-carbon alloys which display, because of higher carbide fractions, a thermal expansion slightly lowered (then a little closer to the chromia one). In addition, it is also possible that the presence of carbides favoured internal oxidation which could, in another way, slightly improve the adherence of chromia on the alloy's surface. But this was not really obvious here.

CONCLUSIONS

Exploiting the cooling parts of thermogravimetric measurements after oxidation at high temperatures during an isothermal stage allowed revealing here possible relationships between, one the one hand the characteristics of the oxidized sample (total amount of external oxide obtained on surface until cooling starts; carbide fractions in the bulk), and on the other hand the characteristics of the scale spallation (temperature loss before beginning, rate of mass loss, fraction of lost oxide). This illustrated the interest to also consider, in addition to the mass gain parabolic kinetic of isothermal oxidation, this part of the measurements files to get a first information about the persistence of the formed oxide protecting the alloy when this one cools down to lower temperatures, before eventually performing real cycling oxidation experiments which are of course much richer in knowledge about resistance against oxide spallation in thermal cycling.

REFERENCES

[1] C.T.Sims, W.C.Hagel; 'The Superalloys', John Wiley and Sons, New York, (1972).
[2] P.Kofstad; 'High Temperature Corrosion', Elsevier applied science, London, (1988).
[3] C.Wagner; Z.Phys.Chem., 21, 25 (1933).
[4] P.Berthod; The Open Corrosion Journal (submitted).
[5] P.Berthod; Ann.Chim.Sci.Mat., 33, 225 (2008).
[6] P.Berthod, P.Lemoine, L.Aranda; Mater.Sci.Forum, 595-598, 871 (2008).
[7] P. Berthod; Int.J.Mater.Res., 99, 265 (2008).
[8] P.Shaffer; 'High-Temperature Materials N°1', Plenum Press, New York, (1964).