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Oxide spallation during cooling from high temperatures affecting carbides-containing nickel-based alloys Part 2 : Case of Ni-Cr-C alloys with addition of tantalum

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ABSTRACT

Thermal cycles may induce a partial or total loss of the oxide scale formed before at high temperature on the external surface of alloys. This loss is logically attributed to the thermal contraction during cooling, which is often more important for alloy than for oxide. The purpose of the second part of this work is to examine the effect of the presence of tantalum on the progress of oxide spallation during cooling for nickel alloys. This was characterized by exploiting the cooling parts of thermogravimetry curves obtained for chromia-forming nickel-based alloys, elaborated by foundry and containing or not tantalum. It appeared that this element, which oxidizes into a more or less continuous sub-cortical second layer, seem deteriorating the adherence of external chromia on alloy. Consequently, at cooling, spallation of the external oxide scale occurs at higher temperatures and its kinetic is accelerated.

KEYWORDS

Nickel alloys;
Carbides;
Tantalum;
High temperature oxidation;
Oxide spallation.

INTRODUCTION

During exposure to high temperature in oxidizing atmospheres, refractory alloys are protected by an oxide scale which prevents fast oxidation[1,2]. In service, this scale is unfortunately lost, partially and even sometimes totally, since temperature does not usually remain constant on long times. Indeed thermal cycling induces differential expansions or contractions between the bulk alloy and the external oxide scale which leads to local or total detachment of the latter. This has detrimental effects on the resistance of the alloy against oxidation since it threatens the duration of the chromia–forming behaviour. If the difference of thermal expansion coefficients between oxide and bulk is of great importance for the spallation phenomenon, another important factor is the adherence of the oxide scale formed on the alloy surface.

In this second part of this work, attention is focused on the possible influence of the presence of another highly oxidable element - tantalum - on the adherence of the external chromia scale. There too, this was studied by analysing the cooling parts of thermogravimetry curves (following isothermal oxidation) obtained for three Ta-containing nickel-based alloys and by comparing with similar results obtained for two Ta-free ternary alloys with the same chromium and carbon contents. The latter results were already presented in the first part of this work[3].

EXPERIMENTAL

The studied alloys are all based on nickel added with almost the same contents in chromium which allows a chromia-forming behaviour. There are two ternary Ni-30Cr-xC (with x equal to 0.2 and 0.4) alloys, and three quaternary alloys Ni-31Cr-0.2C-2Ta, Ni-32Cr-0.4C-2.7Ta and Ni-31Cr-0.4C-5.4Ta (all contents in weight percent). All alloys were synthesized by high frequency induction casting (300kHz, CELES furnace) in inert atmosphere (pure argon, 300mbars). Fusion of pure elements (purity more than 99.9wt.%, average mass of each ingot: 100g) and solidification were achieved in the same cold copper crucible.

The thermogravimetry tests were performed during 50 hours (ternary alloys) or 100 hours (quaternary alloys) using a Setaram TGA 92 thermo-balance (cycle: heating at 20 K min^{-1}, dwell at 1000, 1100 or 1200^{0}C during 50 or 100 hours, cooling at -5 K min^{-1}). Measured masses 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 final sample mass.

After special metallographic preparation[3], the oxidized samples were examined using a Scanning Electrons Microscope (SEM, Philips XL30) in order to observe the oxidized surfaces and distinguish the different types of oxides if any.

RESULTS AND DISCUSSION

Thermogravimetry results recorded during cooling

All the obtained mass gain curves are globally of the type described in the synthetic curve already presented in the first part of this work[3]. All are presented in figure 2 (curves obtained at 1000°C for all alloys), figure 3 (1100°C) and figure 4 (1200^{0}C), and include successively:

- A heating part with initially a mass gain only due to the decrease in Archimede thrust, and after with an additional mass gain really due to oxidation which starts when temperature is become high enough,
- An isothermal part with a mass gain obeying a parabolic* law versus time (*: not visible here in this type of representation),
- A cooling part in which first oxidation goes on slowly and co-exists with the increase in Archimede's thrust due to cooling, and second spallation occurs with a more or less fast mass loss.

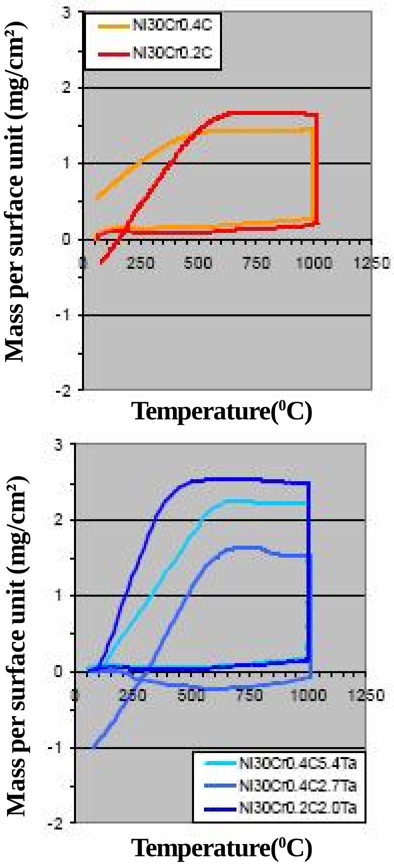

Figure 1: Mass gain plotted versus temperature for the Ta-free (top) and the Ta-containing (bottom) nickel-based alloys for T_{dwell} = 1000°C

However, there are several differences between the curves. Indeed, if the heating parts are almost all of the same type, the isothermal type depends on temperature, on the alloys for which isothermal oxidation is more or less rapid, and on total duration which is 50 hours for the ternary alloys and 100 hours for the quaternary ones. Nevertheless, since in the latter case the mass gain during the second half of duration is significantly lower than the mass gain obtain during the first half (mass gain function of a square root of time according to the parabolic law), it seems that the oxidation of the Ta–containing alloys is faster than the oxidation of the Ta-free alloys at the same temperature. This confirms the order of oxidation parabolic constants Kp with respect

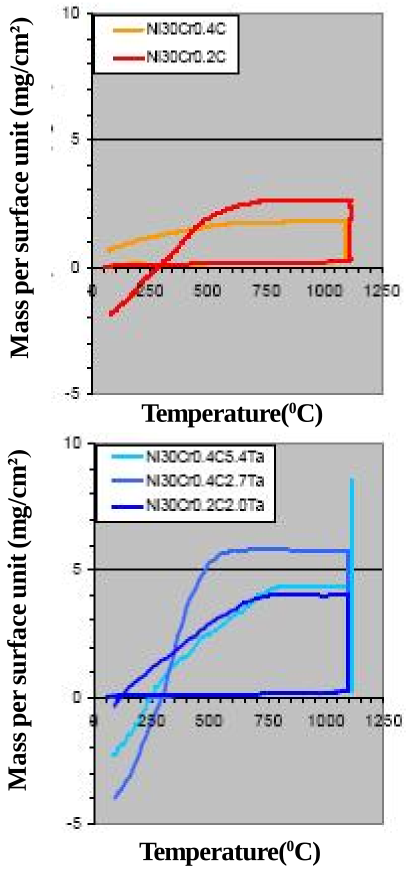

Figure 2: Mass gain plotted versus temperature for the Ta–free (top) and the Ta–containing (bottom) nickel-based alloys for T_{dwell} = 1100°C

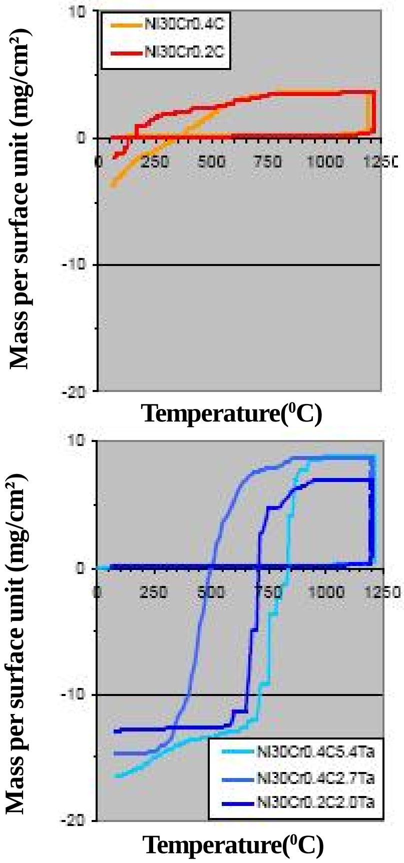

Figure 3: Mass gain plotted versus temperature for the Ta–free (top) and the Ta–containing (bottom) nickel-based alloys for T_{dwell} = 1200°C

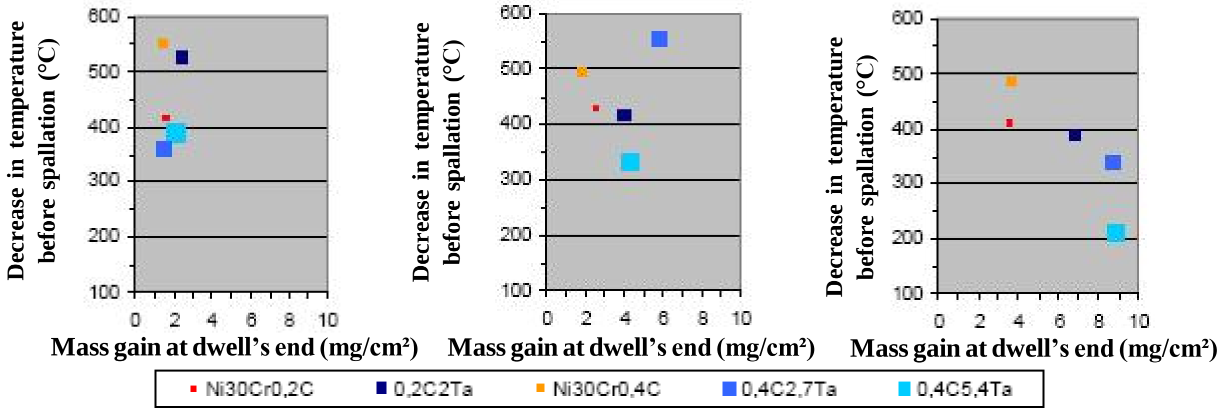

Figure 4: Difference between the dwell's temperature and the temperature at which spallation begins (cooling part), plotted versus the mass gain at the end of the isothermal stage: 1000°C (left hand), 1100°C (middle), 1200°C(right hand)

to the presence of Ta, earlier seen about such alloys[4,5].

Other differences can be also noted about the cooling parts, which are of special interest here. In contrast with ternary cobalt–based alloys with similar chromium and carbon contents[6], these alloys do not present mass gain jump in the cooling parts of their thermogravimetry curves, for most of them (i.e. except for Ni30Cr0.4C2.7Ta after oxidation at 1000°C, figure 1). But differences arise, notably between ternary alloys

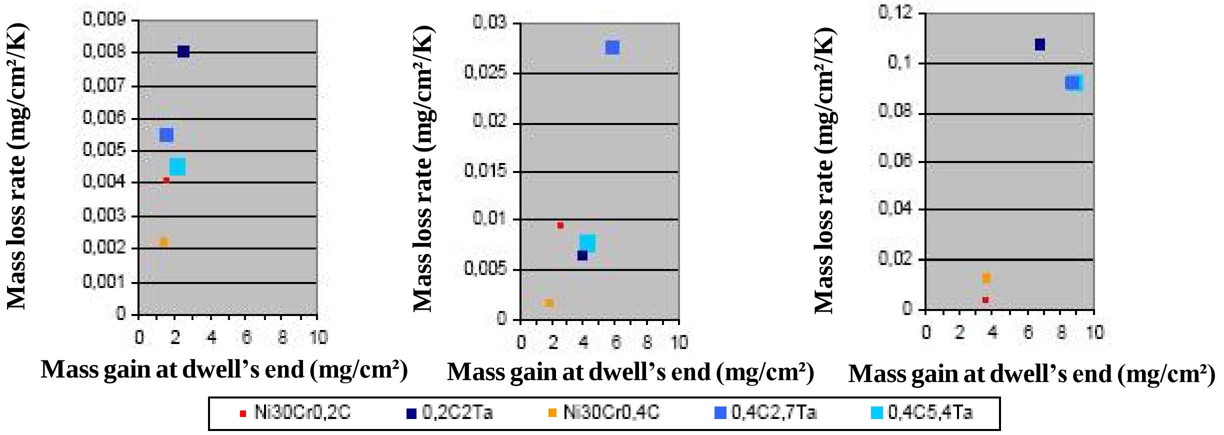

Figure 5: spallation's rate during cooling, plotted versus the mass gain at the end of the isothermal stage: 1000°C (left hand), 1100°C (middle), 1200°C (right hand)

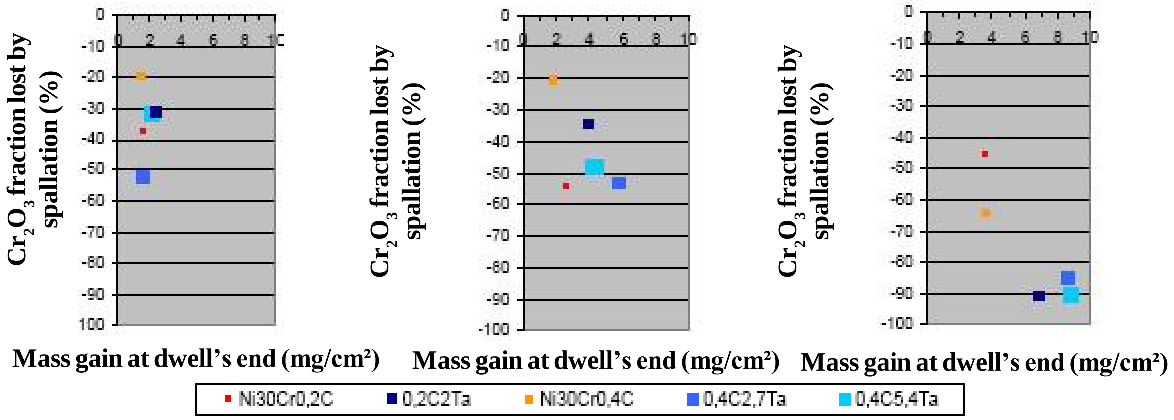

Figure 6: fraction of chromia lost at cooling because of spallation, plotted versus the mass gain at the end of the isothermal stage : 1000°C (left hand), 1100°C (middle), 1200°C (right hand)

and tantalum-containing alloys, when one consider spallation, more precisely the temperature at which a decrease in mass due to the loss of external oxide occurs, and the rate of mass loss with cooling time. The most visible differences concern mainly the total mass loss weighed after return at room temperature, but also the rate of mass loss.

Analysis of the oxide spallation progress

Since one can suppose that temperature of spallation beginning and mass loss rate may depend on the alloy, the nature and the total thickness of the oxide (presence of Ta or not, 50h or 100h of isothermal oxidation), and on the temperature from which cooling started, three characteristics of oxide spallation were studied versus the total mass gain before cooling, as done in the first part of this work[3]. Figure 4 displays the decrease in temperature from the isothermal oxidation one before spallation's start, Figure 5 shows the average mass loss rate in the temperature range where spallation occurred and Figure 6 represents the fraction of external oxide lost by spallation during the whole cooling (the formula used and the hypotheses done were already given in the first part of this work[3]).

It appears first that spallation begins for the ternary alloys at a lower temperature (then for a greater decrease in temperature) than for the tantalum-containing alloys (figure 4), maybe because of a more important mass of oxide (points corresponding to the quaternary alloys are mainly on the right of the graphs). The mass losses are also significantly faster for the Ta–containing alloys than for the Ta–free ones (figure 5). It is true that most of the curves corresponding to the Ta-containing alloys (figures 1-3, bottom) present a fall especially rapid when spallation occurs, notably after oxidation at 1200°C. Consequently, the fraction of oxide lost noticed

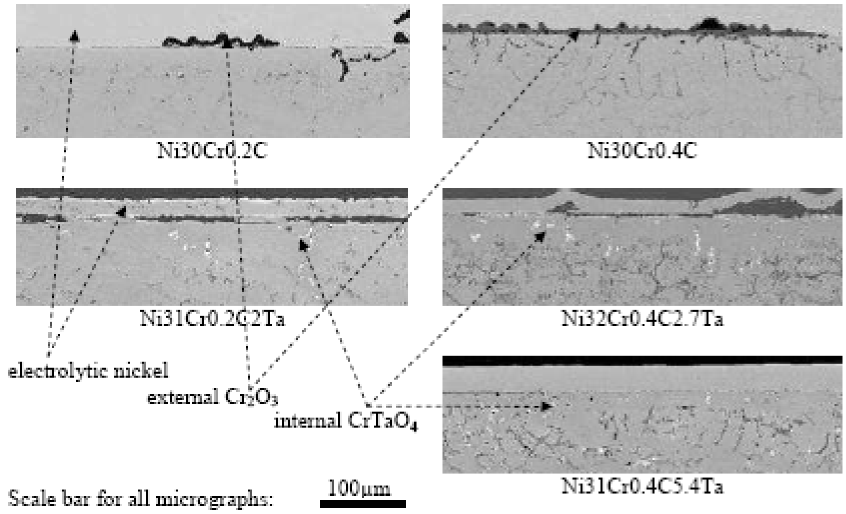

Figure 7: SEM micrographs illustrating the surface state of the oxidized samples (1000°C)

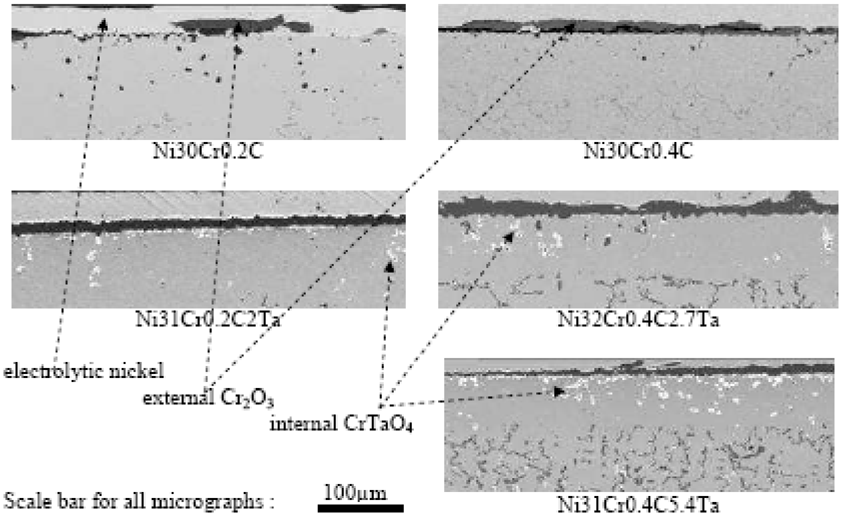

Figure 8: SEM micrographs illustrating the surface state of the oxidized samples (1100°C)

after return to room temperature, is significantly more important for the Ta-containing alloys than for the Ta-free ones, as seen both on thermogravimetry results (figure 6) and on the metallographic cross-sections of the oxidized samples. Indeed, in figures 7-9 (respectively for 1000^{0}C, 1100^{0}C and 1200^{0}C), one can see that some parts of external oxides can be still observed on the surface of the Ni-Cr-C alloys while the Ni-Cr-C-Ta oxides have almost all lost their external oxide scale and can only present their Ta-containing internal oxides ($CrTaO_4$).

General commentaries

For the studied alloys the scale spallation generally begins after several hundreds degrees of cooling. In most cases the mass loss is more or less continuous but it can occur abruptly as seen here with some of the quaternary alloys oxidized at 1200^{0}C. Because of oxide spallation the final mass of the alloys are often lower than initially, although the oxidation phenomenon led to an increase in mass at high temperature.

The studied characteristics of spallation, amount of decrease in temperature before spallation starts or average mass loss rate during spallation, seems being dependent on the mass of oxide initially formed, but it appears that the major factor is here the presence of tantalum and maybe also its content in alloy. Indeed, spallation occurs sooner for the tantalum-containing alloys than for the tantalum-free alloys. Mass loss rates

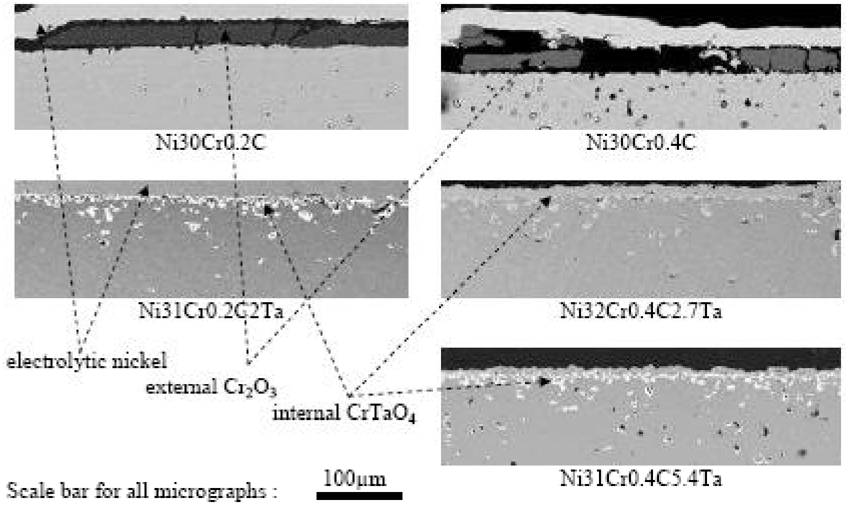

Figure 9: SEM micrographs illustrating the surface state of the oxidized samples (1200°C)

are also faster when tantalum is present (with a tendency to a sudden breakdown for cooling from 1200^{0}C), with consequently a lower oxide fraction as seen with both thermogravimetry and metallography. This is to be compared with the tendency to oxide detachment during isothermal oxidation previously observed for similar alloys[4] (mass gain jumps in curves representing mass gain versus time) but which were not observed for Ta-free ternary alloys with the same carbon and chromium contents[5].

This is not directly related to the total oxide mass obtained at the end of isothermal oxidation (which is effectively generally higher for the quaternary alloys than for the ternary ones), since some quaternary alloys (oxidized at 1000^{0}C, respectively 1100^{0}C) are more affected by spallation than some ternary alloys (oxidized at 1100, respectively 1200^{0}C) for similar mass oxides. One can suppose that it is the internal oxide ($CrTaO_4$, white when observed with the SEM in BSE mode), which is responsible of a bad adherence of the external oxide on the alloy surface. Indeed, this internal oxide tends to partially develop as an inner layer separating the external chromia oxides and the alloy, notably when the Ta content in alloy is high or when the stage temperature is high (figure 9), with tantalum diffusing from an increasing depth in the bulk.

CONCLUSION

The oxide spallation which affects alloys when their temperature decreases after a more or less long oxidation, cannot be really avoided because the thermal contraction of alloys (15 to 20 $\times 10^{-6}$ K^{-1}) is generally faster than the external oxide one (less than 10×10^{-6} K^{-1})[7-9]. But, as seen here with simple chromia-forming nickel-based alloys added or not with tantalum, the phenomenon may be accelerated if an additional highly oxidable minor element is added and forms an oxide separating alloy and chromia, with a detrimental role for the adherence of the protective external scale. It is probable that this effect was here enhanced since tantalum was able to diffuse towards the front oxidation and leads to a second oxide especially present at the interface.

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