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# High temperature oxidation behaviour of cast cobalt-based Cr-rich alloys reinforced by titanium carbides. Part 1: Mass gain kinetics

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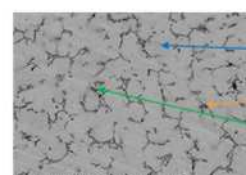
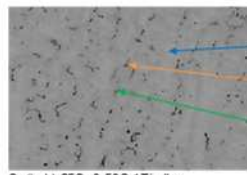
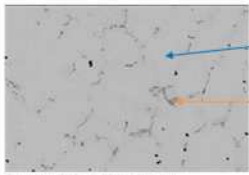
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Cast Co-based Cr-rich alloys were among the earliest metallic alloys used for high temperature applications under oxidant atmospheres [1,2]. The 20 to 30wt.% of chromium they contained were the most often enough to resist oxidation by hot gases and corrosion by molten substances [3]. Since they cannot take benefit from gamma prime precipitation as nickel-based superalloys their mechanical reinforcement must be achieved by solid solution strengthening and/or by primary (solidification) or secondary (heat-treatment) carbides precipitation. The most used carbides are chromium carbides, tungsten or molybdenum carbides and tantalum carbides. More recently, hafnium carbides were also tested in great fractions in cobalt-based [4] but also iron-based [5] and nickel-based [6] chromium-rich cast refractory alloys. Among the best stable carbides at high temperature these are the MC ones which were the most frequently cited: TaC, HfC... TiC is also a metallic monocarbide but this one seems having been rarely or never considered as a strengthening carbide for alloys and superalloys working at high temperature. The purpose of this work is thus to start exploring the microstructures to which the presence of significant atomic contents in C and Ti - close to one another in addition - may lead, this by starting with the cast cobalt-based alloys family. Second, the beginning of discover of the high temperature properties of such alloys will start here with the isothermal high temperature oxidation behaviour. In this first part of the work these are the as-cast microstructures of the obtained alloys which will be on interest, together with the mass gain kinetic during oxidation for several tens hours at temperatures ranging from 1000 and 1200°C in comparison with similar alloys containing either chromium carbides or hafnium carbides. In a second part these are the results of post-mortem characterization of oxidation which will be described.

## Elaboration of the alloys and microstructures' observations

Three alloys whose targeted chemical compositions were Co-25Cr-0.25C-1Ti, Co-25Cr-0.50C-1Ti and Co-25Cr-0.50C-2Ti (all contents in weight percents) were prepared from pure elements (mainly from Alfa Aesar, purity better than 99.9%). These ones were melted together under an inert atmosphere of 300 millibars or pure Argon in the water-cooled copper crucible of a high frequency induction furnace in which both melting and solidification were achieved.

In the as-cast microstructures of the three alloys the matrix is dendritic while carbides are all interdendritic. These carbides are essentially titanium carbides (TiC) in the first alloy (0.25C-1Ti) but chromium carbides are present together with the TiC ones, in the interdendritic spaces. The EDS spot analyses carried out with the SEM indicate that matrix still contains 0.3 wt.% Ti in the cases of the two first alloys (they both contain 1 wt.%Ti, so two-thirds of the whole Ti are present as TiC carbides) and 0.9 wt.%Ti in the third alloy which contains 2 wt.%Ti (so more than the half of the whole Ti is involved in the TiC carbides). Since titanium is not entirely used in TiC carbides the remaining carbon has logically combined with the second main carbide-forming element, chromium, hence the chromium carbides.

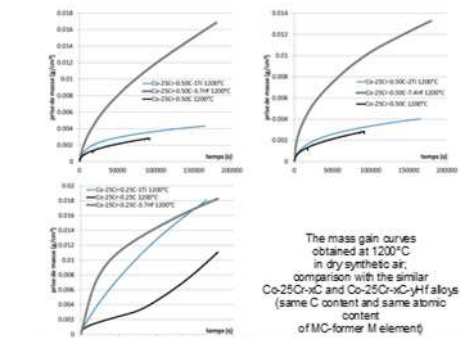
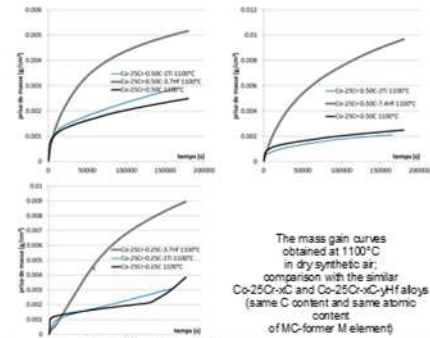
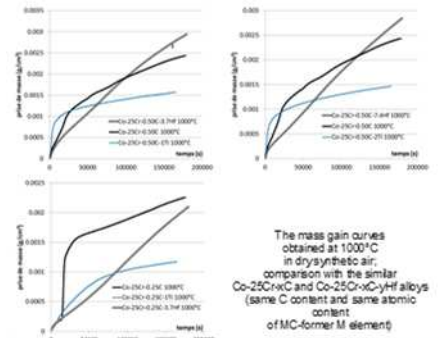


## Thermogravimetry tests

The thermogravimetric analysis tests were performed in dry synthetic air (80%N<sub>2</sub>-20%O<sub>2</sub>, Alphagaz 1) using a SETARAM TGA92 thermo-balance. Their mass variations versus time were recorded. The applied thermal cycles were: heating at +20 °C/min, dwell at 1000°C or 1100°C or 1200°C - 46h, cooling at -5°C/min).

To see if the kinetic of oxidation is parabolic, the mass gain files were plotted versus time. To determine the parabolic constant  $k_p$ , the mass gain per unit area (named  $m$ ) was plotted versus the square root of time. At these high temperature (especially 1100 and 1200°C), the chromia scale (which is the only oxide at the surface of the samples) is volatilized by a re-oxidation reaction into gaseous CrO<sub>3</sub>. This volatilization must be taken into account not to minimize the real oxidation rate. The curves displaying a shape near parabolic and regular enough were then selected for attempting their analysis according to the  $(m \times \text{dm}^2) = k_p \times t$  method [7]. The goal of this method is to find the value of the parabolic constant  $k_p$  without minimization and the value of the chromia volatilization constant  $k_v$ . The curve obtained by plotting the  $(m \times \text{dm}^2)$  versus  $(-m)$  appears linear for values of times high enough (after the transient oxidation),  $k_p$  and  $k_v$  can be read in the equation of this straight line. Indeed,  $k_v$  is the slope and  $k_p$  is the ordinate at the origin of this linear part.

The mass gain curve obtained for the Co-25Cr-0.50C-1Ti alloy (blue) is superposed with the ones earlier obtained with a cast Co-25Cr-0.50C ternary alloy (black) and with a cast Co-25Cr-0.50C-3.7Hf alloy (containing also Hf as HfC carbides, together with some chromium carbides, grey). Similarly the mass gain curve obtained for the Co-25Cr-0.50C-2Ti alloy (blue) is superposed with the ones earlier obtained with a cast Co-25Cr-0.50C ternary alloy (black) and with a cast Co-25Cr-0.50C-7.4Hf alloy (containing again Hf as HfC carbides, grey). This allows distinguishing the specific effect of titanium (and thus of both the presence of Ti in solid solution in the matrix and of interdendritic TiC carbides) by contrast with the ternary alloys for the same chromium and carbon contents, and by contrast with quaternary alloys containing HfC carbides instead TiC and a mixture of chromium carbides and TiC, for the same atomic contents in MC-forming element (the molar mass of Hf is about 3.7 times higher than the Ti one).



The mass gain curves of the Co-25Cr-xC-yTi alloys studied in this work are not really parabolic during oxidation at 1000°C. However, compared to the ones obtained for the ternary alloys which are affected by jumps in mass gain (probable local detachments of the external oxide scales) and of the kinetics more linear than parabolic of the Hf-containing alloys, the Ti-containing alloys behave better. When possible, their curves were treated in order to specify both the parabolic constant  $k_p$  and the  $k_v$  chromia volatilization ones. This allowed obtaining values of  $k_p$  which were not underestimated by mass gains lowered by the loss of chromia by re-oxidation into gaseous CrO<sub>3</sub>. For this temperature of 1000°C, the parabolic constant of the Co-25Cr-0.25C-1Ti is about  $2.4 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ , as is to say equivalent to the one earlier obtained for the ternary Co-25Cr-0.25C alloy ( $2.4 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  too, before the mass gain jump) and to the one obtained for the HfC-containing Co-25Cr-0.25C-3.7Hf one ( $2.5 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  too, before linear oxidation). The curve shape differences are the same between the TiC-containing alloy, the corresponding ternary alloy (tendency to jumps) and the corresponding HfC-containing alloy (tendency to linear oxidation) in the case of the Co-25Cr-0.50C-1Ti. This TiC-containing alloy oxidized with a  $k_p$  value of about  $5 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ , lower than the  $12 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  of the ternary Co-25Cr-0.50C alloy and than the Co-25Cr-0.50C-3.7Hf one ( $13 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ ). The  $k_p$  of the Co-25Cr-0.50C-2Ti alloy was  $4 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ , against  $12 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  for the Co-25Cr-0.50C and  $7 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  for the Co-25Cr-0.50C-7.4 Hf alloy.

The obtained mass gain curves of the Co-25Cr-xC-yTi alloys were more parabolic during oxidation at 1100°C, as the ternary alloys' and HfC-containing alloys' ones. At such high temperature chromia starts to significantly re-oxidize into gaseous CrO<sub>3</sub>, with as result a possible minimization of the mass gain. Thus, when possible, their curves were treated in order to specify both the parabolic constant  $k_p$  and the  $k_v$  chromia volatilization ones (only the corrected  $k_p$  values will be given here). This allowed obtaining values of  $k_p$  which were not underestimated by mass gains lowered by the loss of chromia by re-oxidation into gaseous CrO<sub>3</sub>. For this temperature of 1100°C, the parabolic constant (not corrected because of the not adequate shape of the curve) of the Co-25Cr-0.25C-1Ti is about  $28 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ , higher than the one earlier obtained for the ternary Co-25Cr-0.25C alloy (volatilization-corrected  $19 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ ) but much lower than the one obtained for the HfC-containing Co-25Cr-0.25C-3.7Hf one (volatil.-corrected  $43 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ ). The Co-25Cr-0.50C-1Ti alloy oxidized with a  $k_p$  value of about  $24 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ , lower than the  $41 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  (volat.-corrected) of the ternary Co-25Cr-0.50C alloy and than the Co-25Cr-0.50C-3.7Hf one ( $240 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ , volat.-corrected). The  $k_p$  of Co-25Cr-0.50C-2Ti was  $29 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  (volat.-corrected) against  $41 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  (volat.-corrected) for the Co-25Cr-0.50C and  $470 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  for the Co-25Cr-0.50C-7.4 Hf alloy (volat.-corrected).

All the mass gain curves, obtained at 1200°C in this work for the Co-25Cr-xC-yTi alloys and earlier for the ternary alloys' and HfC-containing alloys' ones, are rather parabolic (just a degeneration into linear was noted for the Co-25Cr-0.25C ternary alloy). All mass gain files were treated in order to specify both the parabolic constant  $k_p$  and the  $k_v$  chromia volatilization ones (here too, only the corrected  $k_p$  values will be given here). For this temperature of 1200°C, the parabolic constant of the Co-25Cr-0.25C-1Ti is about  $800 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ , much higher than the one earlier obtained for the ternary Co-25Cr-0.25C alloy (volatilization-corrected  $140 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ ) but lower than the one obtained for the HfC-containing Co-25Cr-0.25C-3.7Hf one (volat.-corrected  $250 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ ). The Co-25Cr-0.50C-1Ti alloy oxidized with a  $k_p$  value of about  $140 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ , close to the  $130 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  (volat.-corrected) of the ternary Co-25Cr-0.50C alloy and much lower than the Co-25Cr-0.50C-3.7Hf one ( $600 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$ ). The  $k_p$  of Co-25Cr-0.50C-2Ti was  $120 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  (volat.-corrected) close to the  $130 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  (volat.-corrected) for the Co-25Cr-0.50C, and 10 times lower than the  $1330 \times 10^{-12} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  (volat.-corrected) for the Co-25Cr-0.50C-7.4 Hf alloy.

The oxidation of the three studied TiC-containing cobalt-based alloys was generally parabolic at all the temperatures tested here, without tendency to detachment of the oxide scales as often observed for the ternary alloys, and without degeneration to linear oxidation after few hours or tens of hours of isothermal oxidation. In kinetic term they are similar to the ternary alloys while the Hf-containing alloys often oxidized much faster. If the HfC carbides are mechanically particularly interesting in cast chromium-rich alloys, notably for the high temperature creep resistance [8], they also lead to fast oxidation. One does not know at this time whether the TiC carbides will be so efficient in the high temperature strengthening of these alloys, but it clearly appeared here that they seem to do not threaten the oxidation resistance.

In the second part of this work the oxidized samples will be subjected to post-mortem characterization in order to interpret the differences in mass gain kinetic observed here between these TiC-reinforced cobalt-based alloys and the corresponding ternary or HfC-strengthened alloys previously studied.

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