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# Kinetic of oxidation of chromium-rich HfC-containing Co-based and Ni-based alloys between 1000 and 1100°C

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Elodie Conrath, Patrice Berthod. Kinetic of oxidation of chromium-rich HfC-containing Co-based and Ni-based alloys between 1000 and 1100°C. Eurocorr 2014, Sep 2014, Pise, Italy. hal-03476176

**HAL Id: hal-03476176**

**<https://hal.science/hal-03476176>**

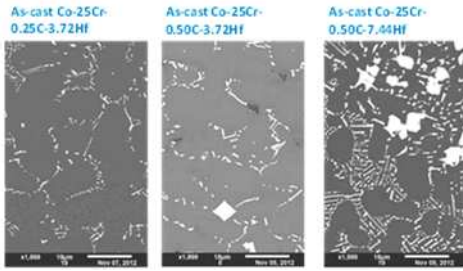
Submitted on 12 Dec 2021

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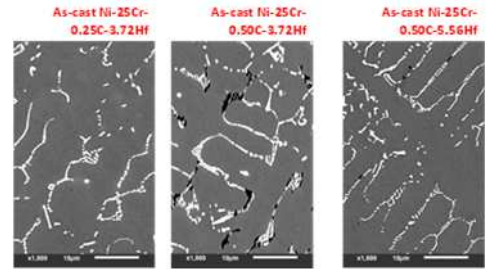
Many cobalt-based superalloys and some nickel-based ones are reinforced by interdendritic carbides for allowing use them in hot conditions [1]. Such carbides must be stable enough at high temperature in term of geometry/shape as well in term of volume fraction. The TaC carbides which reinforce some cobalt-based alloys do not rapidly evolve while TaC carbides are much less stable in chromium-rich nickel-based alloys (and even less stable than the chromium carbides in this second family of alloys [2]). HfC are among the carbides which are more stable at high temperature than the tantalum carbides, much more in the case of the nickel-based alloys [3] and already a little more in the case of the cobalt-based ones [4,5].

Hafnium carbides may potentially lead to nickel-based and cobalt-based alloys very resistant against creep deformation at high temperature but it was recently found that the HfC carbides network may be rather neutral for the behaviour of the nickel-based alloys in oxidation at high temperature [6], but detrimental for the alloys which are based on cobalt [7]. The good stability of the HfC carbides in the same families of alloys can be also exploited at lower temperatures such as 1100 and 1000°C. It appeared that interesting to characterize the behaviour in oxidation at these temperatures of the same alloys already studied at 1200°C [6,7], in order to see if the behaviour of the cobalt-based alloys notably is improved 100°C or 200°C lower.



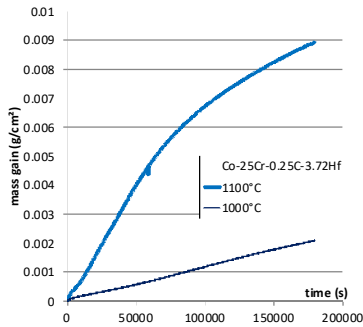
Six alloys were synthesized from pure elements by melting and solidification in the cold copper crucible of a CELES high frequency induction furnace under inert atmosphere of pure argon.

The thermogravimetry tests were performed using a TGA 92 thermobalance (SETARAM). The isothermal parts were plotted versus time for observation of the general shape (parabolic or not). They were also plotted as  $m \times dm/dt = f(m)$  to specify the true parabolic constant  $K_p$  and the liner constant  $K_v$  characterizing the volatilization of chromia (1100 and 1200°C), according to the  $(m \times dm/dt = K_p - K_v \times m)$  method [8].



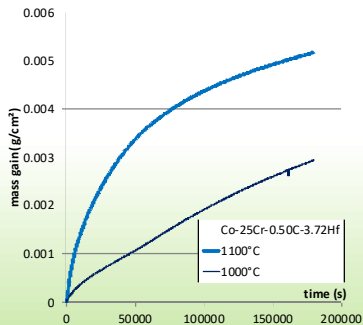
As-cast microstructures of the three HfC-containing cobalt-based alloys

As-cast microstructures of the three HfC-containing nickel-based alloys

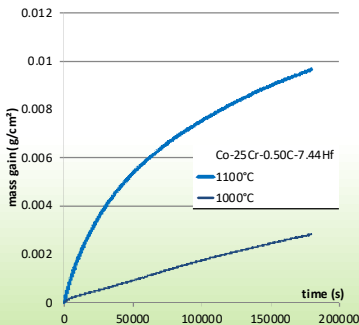


The Co-25Cr-0.25C-3.72Hf alloy oxidized quickly at 1100°C with a rather long linear regime which finishes to be followed by a seemingly parabolic part. The  $(m \times dm/dt = K_p - K_v \times m)$  treatment led to  $K_p = 40 \times 10^{-10} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  and  $K_v = 2.70 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$  (method de Berthod in [8]) which are rather high values for this temperature. At 1000°C the kinetics is almost linear.

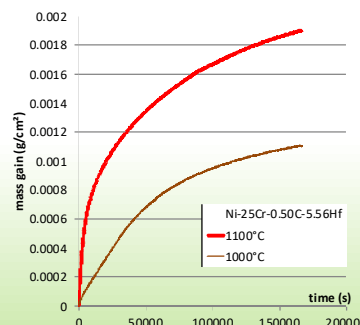
The Co-25Cr-0.50C-3.72Hf alloy oxidized at 1100°C a little slower than the previous alloy at 1100°C. The  $(m \times dm/dt = K_p - K_v \times m)$  treatment led to  $K_p = 2.40 \times 10^{-10} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  and  $K_v = 36 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ .



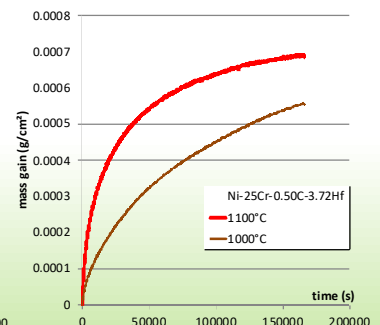
At 1000°C the kinetics is here too almost linear. The linear regime is also observed for the Co-25Cr-0.50C-7.44Hf alloy oxidized at 1000°C. At 1100°C the regime is parabolic, with  $K_p = 7.0 \times 10^{-10} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  and  $K_v = 2.70 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ .



For the Ni-25Cr-0.50C-3.72Hf alloy the constants are  $K_p = 2 \times 10^{-10} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  and  $K_v = 20 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$  at 1000°C. At 1100°C these constants become  $K_p = 6 \times 10^{-10} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  and  $K_v = 100 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ .

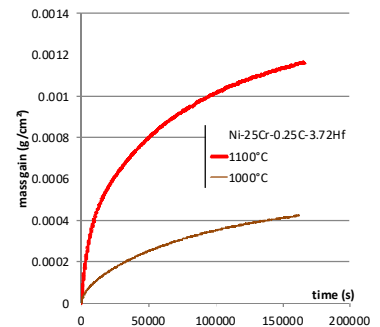


For the Ni-25Cr-0.50C-5.56Hf alloy the obtained values are  $K_p = 9 \times 10^{-10} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  and  $K_v = 60 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$  at 1000°C. At 1100°C these constants become  $K_p = 35 \times 10^{-10} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  and  $K_v = 150 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ .



By comparison with alloys which are really chromia-forming the cobalt alloys have led to either linear kinetics (1000°C) or to parabolic but fast kinetics (1100°C). It is possible that so high hafnium contents (chosen at these values to obtain dense HfC carbides precipitations) are at the origin of these rapid oxidations. However it is true that the alloys of this study, with only 25 wt.% of chromium, are maybe a little too poor in chromium.

For the nickel alloys, which also contain 25 wt.%Cr, the observed behaviours are very good (final mass gains an order of magnitude lower than the similar cobalt alloys of this study) and particularly slow oxidations were seen for these temperatures. By comparison with Hf-free alloys containing the same chromium quantities, it appears possible that Hf played, even with so high contents, a beneficial role for the oxidation resistance of the alloys.



The parabolic constant obtained for the Ni-25Cr-0.25C-3.72Hf alloy is  $K_p = 0.6 \times 10^{-10} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  at 1000°C ( $K_v$  negligible). For 1100°C the constants were  $K_p = 12 \times 10^{-10} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$  and  $K_v = 87 \times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ .

Obtaining dense HfC carbides reinforcing network led to Hf contents significantly higher than usual. This may be responsible of the bad oxidation behaviour observed for the cobalt alloys even for these two temperatures lower than the 1200°C at which they were previously tested. The very high temperature (1200°C) which was pointed out in previous works is not the single responsible of this based oxidation resistance. Besides Hf (which is not necessarily favourable when present in so high quantities) the chromium content a little too low for cobalt-based alloys probably merits to be augmented. Inversely, the nickel-based alloys present simultaneously dense HfC carbides and good resistance against high temperature oxidation. They appear as being ready for use at high temperature under mechanical stress in oxidant atmospheres.

## References

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