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# Carbide transformations occurring between 1000 and 1100°C in the sub-surface of a Ni-25Cr-0.50C alloy induced by hot oxidation

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► **To cite this version:**

Patrice Berthod, Elodie Conrath. Carbide transformations occurring between 1000 and 1100°C in the sub-surface of a Ni-25Cr-0.50C alloy induced by hot oxidation. Eurocorr 2014, Sep 2014, Pise, Italy. hal-03518169

**HAL Id: hal-03518169**

**<https://hal.science/hal-03518169>**

Submitted on 9 Jan 2022

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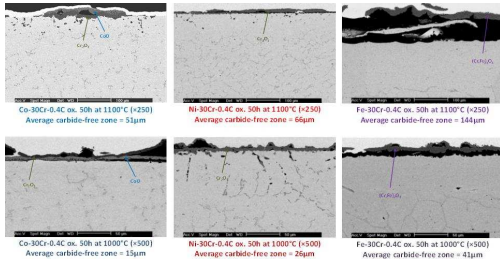
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Alloys and superalloys elaborated by foundry practice are often strengthened by carbides. They constitute an important family of refractory alloys for applications at high temperature [1]. The metallic carbide-forming elements present in the reinforcing carbides are easily oxidable [2]. When they are used in hot conditions in aggressive environments, such alloys are subjected to changes of the carbides initially present in the sub-surface [3,4]. These changes are induced by high temperature oxidation occurring on surface. Such microstructure modifications may possibly modify the local refractoriness [5] as well as the local mechanical properties in sub-surface.

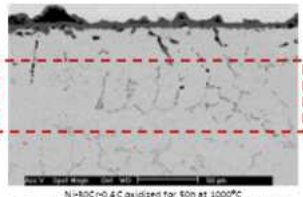
These phenomena can be of different types: (eventually) development of a carbide-free zone (case of alloys reinforced by chromium carbides and/or TaC carbides) or not (case of HfC-reinforced alloys), local coarsening/nature change of the carbides initially present, precipitation of new ones ...

This study focuses on the oxidation-induced phenomena encountered in the sub-surfaces by ternary Ni-Cr-C alloys, with additionally the study of the effect of the temperature and duration of oxidation. The phenomena are interpreted using thermodynamic calculations [6,7].

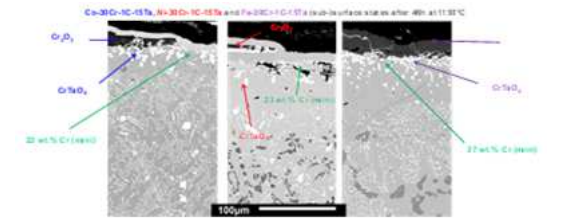
## Several examples of sub-surface phenomena happened during the high temperature oxidation of carbides-containing alloys



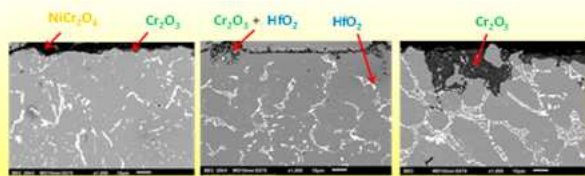
Example 1: Surface and sub-surface states of the M-30Cr-0.4C alloys after oxidation: carbide-free zones in all cases and phenomena concerning carbides in the case of the Ni-30Cr-0.4C after oxidation for 50h at 1000°C



Example 2: Development of a carbide-free zone but with coarsening of the intermediate carbides and precipitation of new ones



Example 3: external and internal oxidation with development of a carbide-free zone for three M-30Cr-1C-15Ta cast alloys oxidized during 46 h at 1150°C; outwards diffusion of Cr and Ta atoms

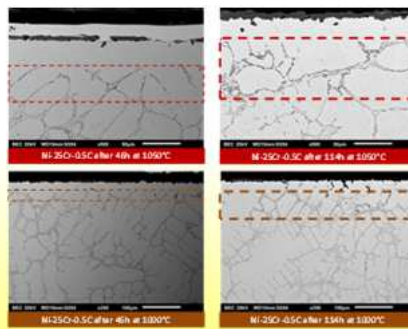


Example 4: internal (and external) oxidation only (no development of carbide-free zone) for three Ni-25Cr-based (HfC carbides)-containing cast alloys oxidized during 46 hours at 1150°C; no Hf diffusion

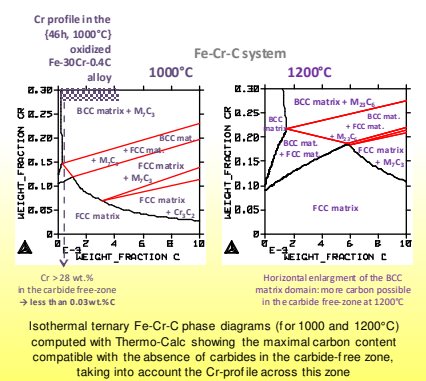
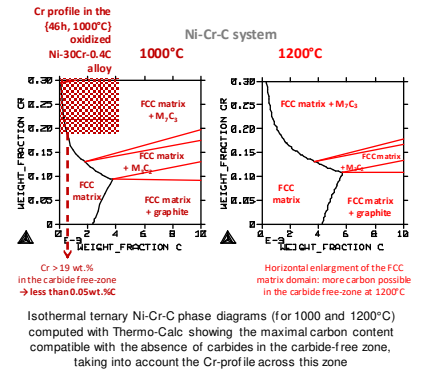
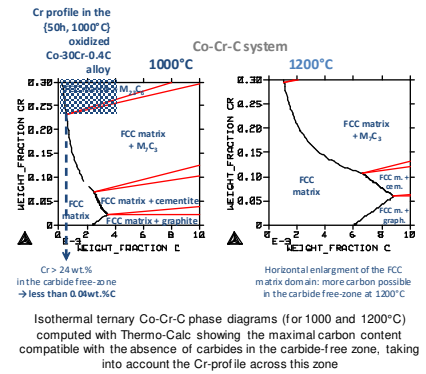
## Use of thermodynamic calculations for interpreting the phenomena

In most cases, the carbides disappear during oxidation, progressively from the {external oxide, alloy} interface. As demonstrated by thermodynamic calculations these growing carbide-free zones are much poorer in carbon than the initial alloy (here 0.4 or 0.5 wt.%) since the maximal carbon content value is only the tenth part of the initial one. Furthermore it is probably almost inexistent in this area. The carbon atoms initially present as carbides have probably diffused towards the oxidation front to be oxidized into gases.

However, in some cases, it seems that a part of this carbon quantity has, on the contrary, diffused inwards to promote the appearance of new quantities of carbide deeper, either by coarsening the present ones, or by precipitating new ones finer. The reason of this inversion of diffusion direction remains to explain, but one can guess that the resulting local microstructure modifications may have consequences on the mechanical, thermal expansion and refractoriness properties of the concerned alloys.



Evolution with time of the intermediate zone where carbides are modified (coarsened for example) at 1000°C and 1050°C for a cast Ni-25Cr-0.25C alloy



Oxidation thus induces curious microstructure phenomena in the sub-surface of the carbide-strengthened alloys. Some of them (new carbides zone) are much more difficult to interpret/explain than the other (carbide-free zone notably). Obviously, in addition to temperature-dependent, these later phenomena are also time-dependent, as suggested by the additional tests with longer durations. Further work may consist in new duration increasing to follow further the evolution with time of this particular intermediate zone. In parallel one can also wonder how the oxidizing atmosphere may influence these phenomena (e.g. presence of water vapour in air).

## References

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