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Thermodynamic calculations used for characterizing the sub-surface changes induced by high temperature oxidation for carbides-reinforced alloys



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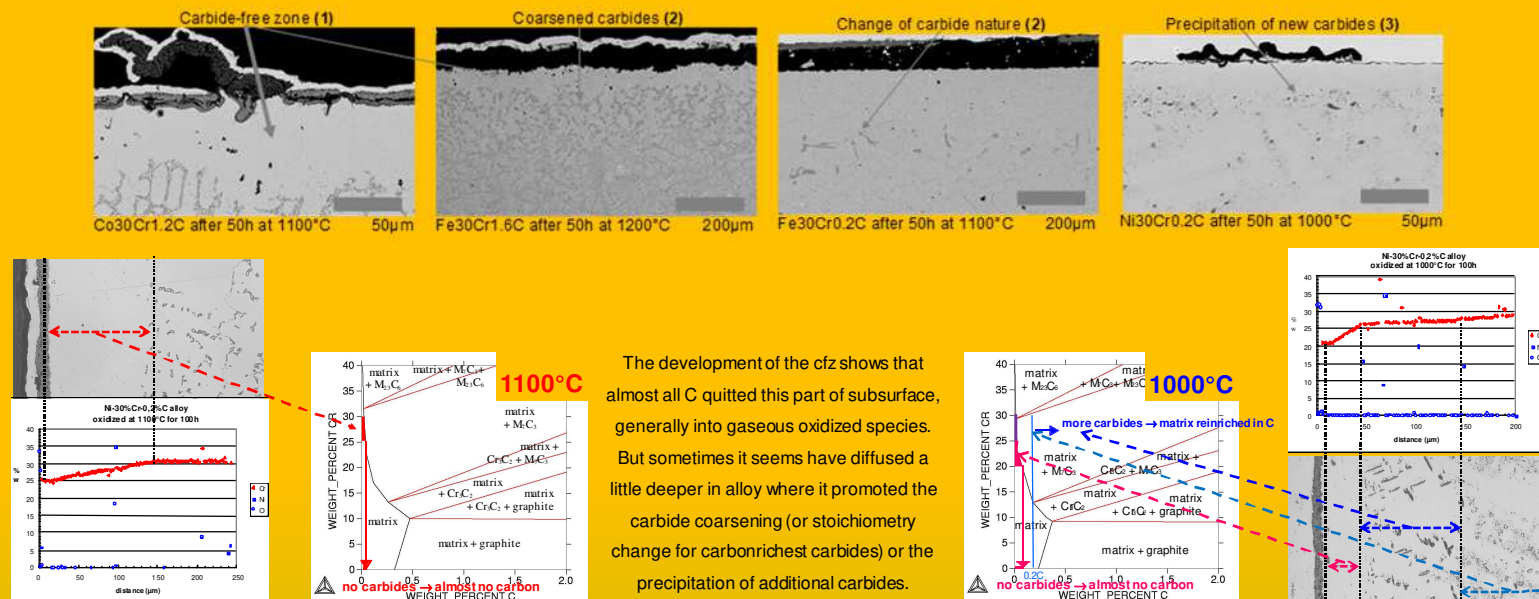
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To achieve sufficient mechanical properties for high temperature applications many refractory cast alloys are strengthened by carbides. When these ones are oxidized at high temperature their subsurface microstructures evolve. There is generally a disappearance of carbides from surface over a depth which increases with temperature and time while, in some conditions, curious phenomena occur for carbides in an area separating carbide-free zone and bulk (coarsening, stoichiometry change, precipitation of additional carbides). In addition, iron alloys may also know modification of matrix nature in the zone affected by oxidation, due to local chemical changes. The aim of this work is to list the types of subsurface modifications (concerning carbides only) induced by high temperature oxidation, and to interpret these local microstructure phenomena by using thermodynamic calculations.

Some examples of sub-surface microstructure changes induced by oxidation at high temperature:

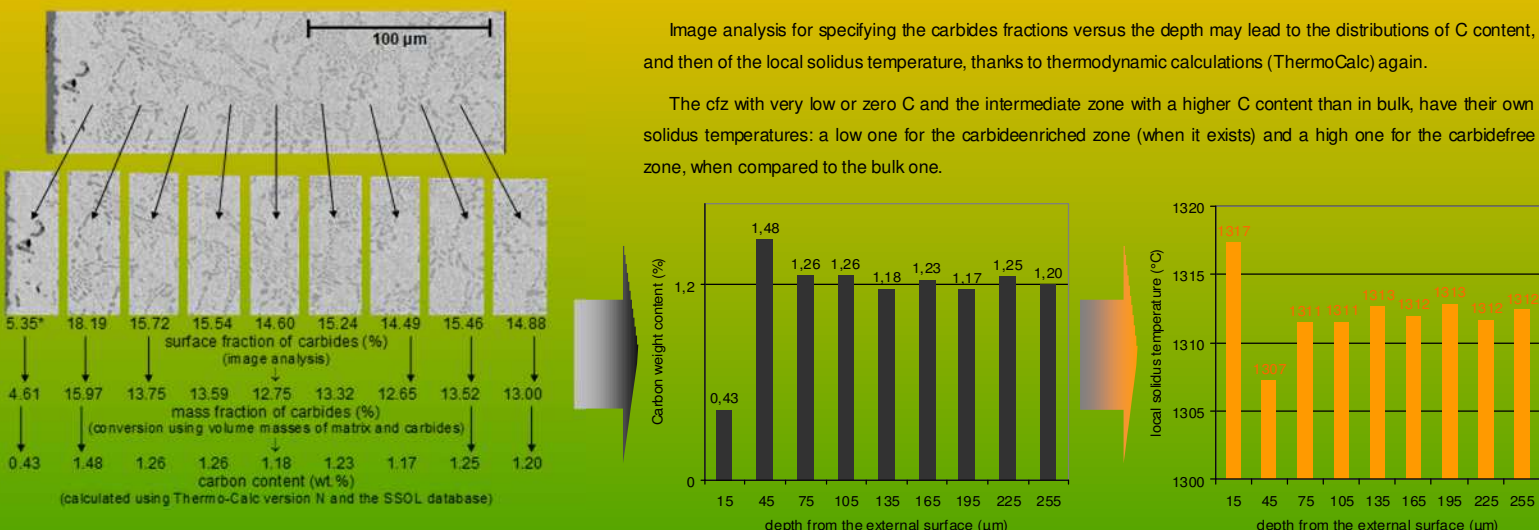
existence or not of an outer zone (1) in which carbides have disappeared (carbide-free zone, "cfz"), modifications of the already existing interdendritic carbides concerning their morphology / surface fraction or their apparent composition (2), existence of new carbides precipitated in matrix in a zone separating the carbide-free zone and the unmodified bulk (3)



The development of the cfz shows that almost all C quitted this part of subsurface, generally into gaseous oxidized species. But sometimes it seems have diffused a little deeper in alloy where it promoted the carbide coarsening (or stoichiometry change for carbon richest carbides) or the precipitation of additional carbides.

Image analysis for specifying the carbides fractions versus the depth may lead to the distributions of C content, and then of the local solidus temperature, thanks to thermodynamic calculations (ThermoCalc) again.

The cfz with very low or zero C and the intermediate zone with a higher C content than in bulk, have their own solidus temperatures: a low one for the carbide-enriched zone (when it exists) and a high one for the carbide-free zone, when compared to the bulk one.



Thus, in addition to the development of oxides layer over the external surface and sometimes internal oxides growth, oxidation at high temperature promotes several subsurface microstructure modifications. Among them there are sometimes curious phenomena concerning deeper carbides, obviously induced by a not outward but inward diffusion of carbon released by disappearing carbides. The growing carbide-free zone, which always acts, may be considered as not desirable for the alloy surface because of a decrease in hardness and probably in wear resistance; but it can be also considered as an especially refractory skin which can prevent emergence of molten alloy as in case of sudden significant increase of temperature in service.