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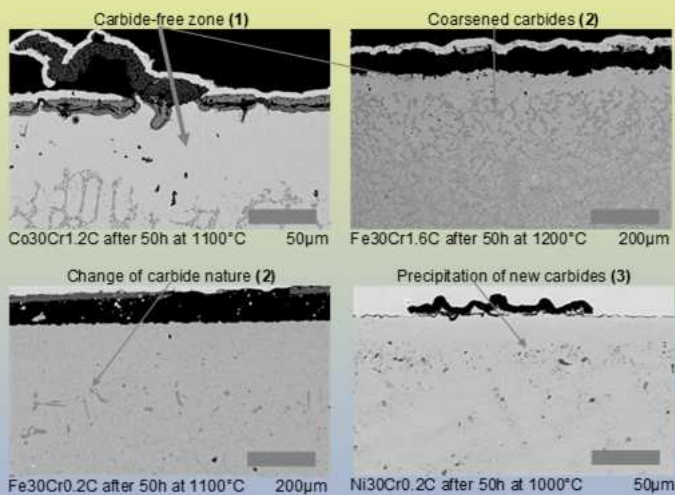
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# Several possible consequences of high temperature oxidation for the subsurface microstructure of carbides-containing alloys

Many refractory cast alloys are strengthened by carbides to achieve sufficient mechanical properties for high temperature applications. When they are oxidized at high temperature their subsurface microstructures are changing. Carbides generally disappear from surface over a depth increasing with temperature and time while, sometimes, carbides undergo modifications in an area separating carbide-free zone and bulk (coarsening, stoichiometry change, precipitation of new ones). In some cases, a change of matrix in iron alloys can also be encountered 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 attempt to correlate them to the identity of the base elements, the initial carbide density and the exposure temperature.

The subsurface modifications which were considered are illustrated below:

existence or not of an outer zone (1) in which carbides have disappeared, modification of the already existing interdendritic carbides, about their qualitative surface fraction or their apparent composition (2) and existence of new carbides precipitated in matrix in a zone separating the carbide-free zone and the unmodified bulk (3).



It appears that almost all alloys display a carbide-free zone ("cfz"). Its depth increases when T increases and decreases when the C content increases, and tends to be higher for Fe alloys than for Ni alloys, and higher for Co alloys than for Fe alloys.

About the coarsening of carbides (or their change of stoichiometry) in an area separating the cfz and the unaffected bulk, the Ni alloys concerned by these phenomena are mainly the ones with the low or medium C contents, and for the lowest T. This does not seem occurring in the Co alloys, and only at the highest T for the Fe alloys.

New secondary carbides precipitated in matrix, also in an area between the cfz and the bulk, in rare cases. This occurred in Fe30Cr-0.4C at 1200°C and for the Ni30Cr0.2C at 1000°C.

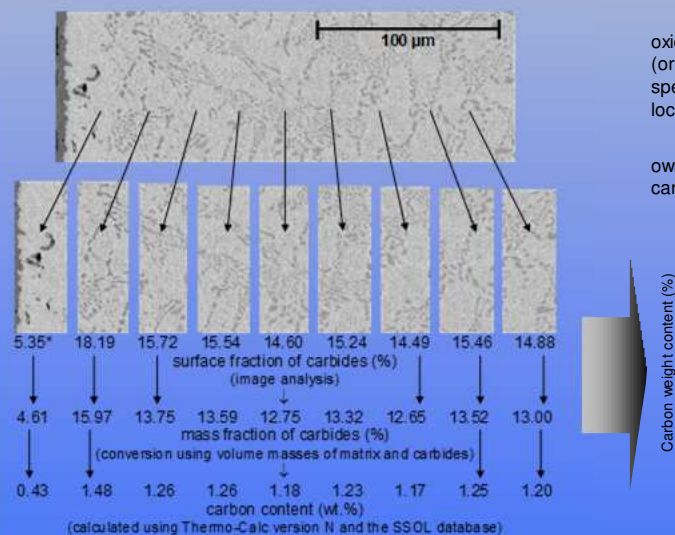
Nickel alloys	T(°C)	0.2C	0.4C	0.8C	1.2C	1.6C	2.0C
Carbide-free zone (YES/no)	1200	190µm	←	YES	→	55µm	
	1100	80µm	←	YES	→	30µm	
	1000	15µm	←	YES	→	10µm	
Coarsened carbides or change of their nature (YES/no)	1200	yes?	yes?	no	no	no	no
	1100	yes?	yes?	yes?	no	no	no
	1000	no	YES	yes?	yes?	no	no
Precipitated carbides (YES/no)	1200	no	no	no	no	no	no
	1100	no	no	no	no	no	no
	1000	YES	no	no	no	no	no

Cobalt alloys	T(°C)	0.2C	0.4C	0.8C	1.2C	1.6C	2.0C
Carbide-free zone (YES/no)	1200	no carbide			115µm	← YES →	105µm
	1100	30µm			← YES →	40µm	
	1000	65µm			← YES →	20µm	
Coarsened carbides or change of their nature (YES/no)	1200	*	no	**	no	no	no
	1100	*	yes?	no	no	no	no
	1000	*	yes?	no	no	no	no
Precipitated carbides (YES/no)	1200	*	no	**	no	no	no
	1100	*	no	no	no	no	no
	1000	*	no	no	no	no	no

\* no carbides were seen, \*\* idem, because fast oxidation

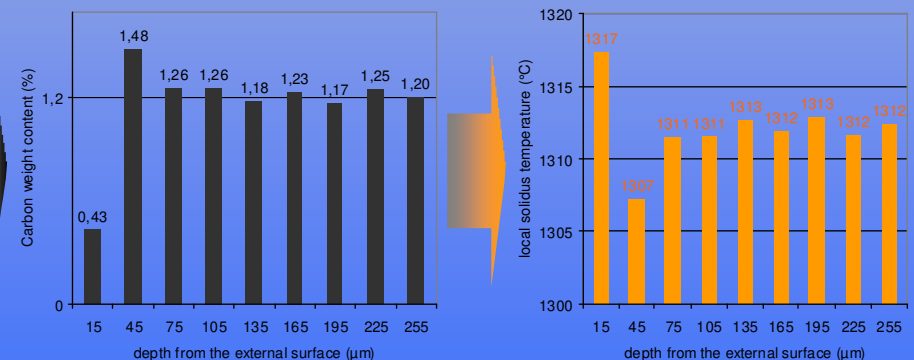
Iron alloys	T(°C)	0.2C	0.4C	0.8C	1.2C	1.6C	2.0C
Carbide-free zone (YES/no)	1200	no c.			330µm	← YES →	40µm
	1100	195µm			← YES →	30µm	
	1000	120µm			← YES →	15µm	
Coarsened carbides or change of their nature (YES/no)	1200	*	yes?	YES	no	YES	no
	1100	YES	no	YES	no	no	no
	1000	*	YES	no	no	no	no
Precipitated carbides (YES/no)	1200	*	no	no	no	no	no
	1100	no	no	no	no	no	no
	1000	*	no	no	no	no	no

\* no carbides were seen



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

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.



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, but also a more frequent growing carbide-free zone. If the latter may be considered as not desirable for the alloy surface because of a decrease in hardness and probably in wear resistance, this carbide-free zone can be considered as an especially refractory skin which can prevent emergence of molten alloy areas in case of sudden significant increase of temperature in service.