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Behaviour of carbides-rich Co, Ni or Fe (bal.) -30Cr -2.5 to 5wt.%C ternary alloys in oxidation at high temperature

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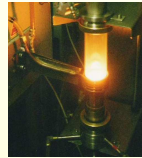
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Cast cobalt-based, nickel-based and iron-based alloys are widely used for numerous applications, and notably their chromium-rich versions are often considered in different domains, among them aeronautics for which chromium allows the alloys well resisting against high temperature oxidation and corrosion. Carbon can be added in great quantities to these alloys in order to obtain high fractions of chromium carbides to achieve high levels of hardness and of good resistance against wear phenomena. In service the wear-solicited materials or coatings may reach high temperatures, because friction-induced heating. They can be then affected by oxidation by hot gases and their resistance to this deterioration needs to be better known especially for versions of such alloys obtained by classical foundry way for which this was seemingly not extensively studied. The aim of the present work is precisely to study the behaviour in high temperature oxidation in air of chromium carbides – rich alloys based on cobalt, nickel and iron, elaborated by conventional casting.

Elaboration of the alloys

18 alloys, 6 {Co-30wt.%Cr}+C, 6 {Fe-30wt.%Cr}+C and 6 {Ni-30wt.%Cr}+C, with %C = to 2.5 (alloys "Co25", "Fe25" and "Ni25"), 3.0 ("Co30", "Fe30", "Ni30"), 3.5 ("Co35", "Fe35", "Ni35"), 4.0 ("Co40", "Fe40", "Ni40"), 4.5 ("Co45", "Fe45", "Ni45") and 5.0wt.% ("Co50", "Fe50", "Ni50") were elaborated by foundry under argon (Ar), using a high frequency induction furnace (CELES).

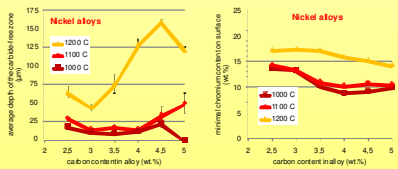
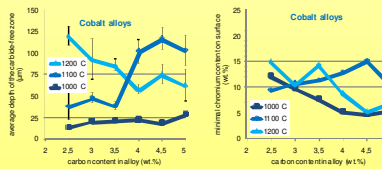
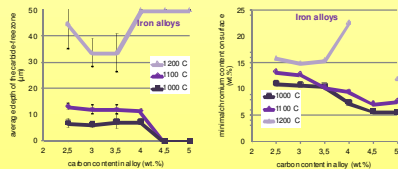
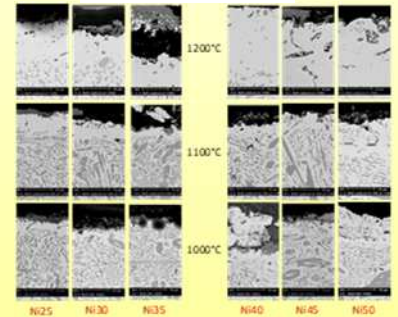
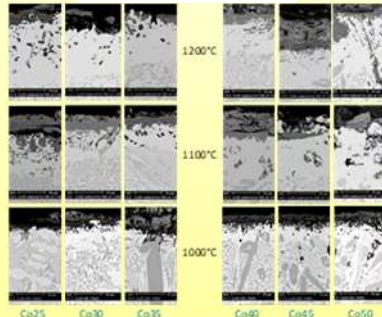
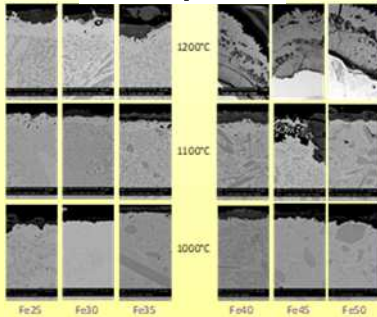
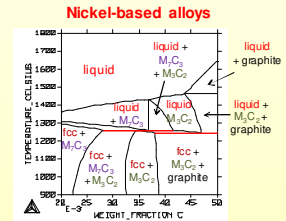
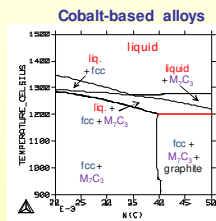
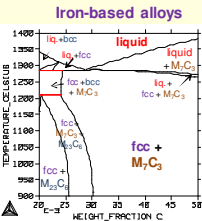
Fusion and solidification were achieved in the water-cooled copper crucible of the furnace. The masses of the obtained ingots were about 40g. Compact samples of about 125 mm³ were cut to obtain, per ingot, one sample for the examination of the as-cast microstructure, and the three others destined to the oxidation tests.



High temperature oxidation tests

The samples were exposed to the laboratory air at 1000°C, 1100 or 1200°C for 50 hours in a resistive tubular furnace, followed by air quenching. After embedding and polishing a Scanning Electron Microscope (PHILIPS XL30) was used for metallographic observations in the Back Scattered Electrons mode.

WDS measurements (Wavelength Dispersion Spectrometry) were performed using a CAMECA SX100 microprobe (Co and Ni alloys) and a JEOL Scanning Electron Microscope equipped with a WDS device (Fe alloys), in the oxide scales and the alloys' sub-surfaces affected by oxidation to better know the oxides' natures and the minimal chromium content on extreme surface.



The Fe25 alloy displays a microstructure still hypoeutectic with presence of matrix dendrites in addition to the {matrix + carbide} eutectic. The Fe30 alloy is near eutectic and the Fe35, Fe40, Fe45 and Fe50 alloys are all hyper-eutectic with presence, in addition to the same eutectic compound, of coarse and acicular pro-eutectic carbides.

Fe40, Fe45 and Fe50 were catastrophically oxidized after 50h at 1200°C. Their oxide scales were exceptionally thick and all the chromium carbides were lost consequently to the outward diffusion of all carbon and its oxidation into gaseous species. Concerning all the oxidized alloys in general, the identified oxides present on surface were Cr₂O₃ (chromia), (Cr,Fe)₂O₃ (with Cr and Fe in equal proportions or with preponderance of Cr or of Fe) and Fe₂O₃ (hematite). The Cr₂O₃ and Fe₂O₃ oxides were clearly differentiated on samples oxidized at 1000°C, (Cr,Fe)₂O₃ with preponderance of Cr and (Cr, Fe)₂O₃ with preponderance of Fe were often observed on alloys oxidized at 1100°C, and (Cr,Fe)₂O₃ with almost equal quantities of Cr and Fe existing beside Cr₂O₃ and/or Fe₂O₃ (separating the two latter) were often seen on samples oxidized at 1200°C.

The cobalt-based alloys are hypoeutectic (Co25 and Co30: matrix dendrites + interdendritic {matrix+carbides} eutectic), almost eutectic (Co35) or hyper-eutectic (Co40 to Co50: {matrix+carbides} eutectic + coarse acicular pro-eutectic carbides). The two carbon-richest alloys contain in addition some graphite particles. All carbides are Cr₇C₃.

For all the Co alloys the damage by oxidation is rather serious (deep carbide-free zones, external oxides of different types and porosity degrees, internal oxidation and voids in sub-surface) although no real catastrophic oxidation was noticed (neither exceptionally thick oxides, nor carbides disappearance from surface to center). Oxidation is more severe for a higher temperature and for a higher carbon content in the alloy. Here too the external oxides were partly lost during cooling. WDS measurements showed that chromia (inner oxide) is present in all cases, but often with other oxides (CoO and spinel CoCr₂O₄, outer oxides).

The nickel alloys are all hypereutectic, with a {matrix+carbide} eutectic compound and coarse pro-eutectic carbides, and graphite for the three carbon-richest alloys, Ni40, Ni45 and Ni50. Carbides are mainly Cr₃C₂ in all alloys but Cr₇C₃ are also present in the two lowest-carbon alloys: Cr₇C₃ with Cr₃C₂ in Ni25 at 1000 and 1100°C, and only Cr₇C₃ at 1200°C in Ni25 and Ni30.

Chromia was always present but other types of oxides were also seen and internal oxidation (generally Cr₂O₃ too) can be observed in most of the oxidized alloys. Several coarse chromium carbides emerging on surface were obviously oxidizing. Oxidation induced for all alloys the development of a carbide-free zone, deeper for a higher temperature and which increases when the carbon content increases, probably because of the faster oxidation for a higher temperature and for a higher carbon content. For 1000/1100°C and for the carbon-richest alloys the chromium content on extreme surface is the lowest (around 10wt.%Cr) and this let think that, as for the two other families of alloys, oxidation may become catastrophic soon after the 50h of these oxidation tests.

Finally all these hard alloys very rich in carbon, mainly present as carbides but also as graphite in some cases, displayed a rather good resistance against oxidation by air at temperatures as high as 1200°C and under. Except the three carbon-richest iron alloys exposed to the very high temperature of 1200°C, the behaviour of the alloys was rather good at least during 50 hours, as shown by the presence of external chromia (but, it is true, more or less mixed with other not so protective oxides). The low chromium contents in matrix, due to the consumption of a great part of this element when the numerous carbides formed during solidification, was obviously corrected during high temperature oxidation by an enrichment of the matrix with Cr coming from the carbides dissolving deeper and deeper (carbide-free zone development). The presence of graphite in the C-richest cobalt-based and nickel-based alloys did not provoke a catastrophic oxidation although this free carbon especially exposed to oxidation may generate great volumes of CO_x gases able to perturb the continuity of the growing external protective scale. To finish one can also notice that the most external parts of these alloys are replaced by carbide-free zones which are much softer than the carbides-rich bulk alloys. This can be a problem to maintain a good wear resistance on surface.