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Study of the behavior in oxidation at high temperature of Ni, Co and Fe-base alloys containing very high fractions of carbides

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Abstract. Nine cast alloys reinforced by very high fractions of carbides, Ni-30Cr-xC, Co-30Cr-xC and Fe-30Cr-xC with x varying from 1.2 to 2.0, were tested in oxidation at high temperature between 1,000 and 1,200°C in air for 50 hours. After oxidation, their surfaces and sub-surfaces were characterized. Even for very high carbon contents, the chromia-forming behaviour of the nickel alloys is kept. The oxidation modes of the cobalt alloys and iron alloys are not changed compared to low carbon alloys of these families. The differences of diffusion easiness of chromium in matrix, between nickel alloys, cobalt alloys and iron alloys are the same as for alloys with lower carbon contents, as suggested by the lower chromium gradients in the nickel alloys compared to the two other alloy types. Sub-surface microstructure transformations due to oxidation were observed in some cases (coarsening of carbides due to an inwards diffusion of carbon, change of the sharing between BCC-FCC of iron matrix due to outwards diffusion of chromium). Catastrophic oxidation never occurred for these alloys during the 50 hours of exposition to air at high temperature.

Introduction

Some of the alloys or superalloys for uses at high temperature contain significant quantities of carbides, the role of which is essentially to achieve sufficient mechanical properties [1,2]. In alloys which contain chromium to be resistant against high temperature corrosion [3], some of the carbides may involve a part of chromium since this one is a carbide-former element. Thus, for a given chromium content, which is generally 30%wt or lower, high carbides fractions lead to a new distribution of chromium in alloy, with an especially great content in grain boundaries and therefore an impoverishment in matrix. This can be of great importance for the high temperature oxidation behaviour of the alloys.

In this work the deterioration, by oxidation in air at high temperature, of the surface and the sub-surface of three families of alloys (Ni-base, Fe-base and Co-base), all containing 30%wt of chromium and several high contents of carbon, was studied by metallographic examinations after oxidation tests.

Experimental Procedures

Elaboration of the alloys and oxidation tests. Nine alloys M-30%Cr-x%C (x=1.2, 1.6 and 2.0), the base elements of which are the ones of most of the conventionally cast superalloys for high temperature applications, i.e. nickel, cobalt and iron, were elaborated by High Frequency induction melting (of graphite and pure Ni, Co, Fe and Cr, > 99.9%wt., Alfa Aesar) in an inert Argon

atmosphere. Solidification occurred in the water-cooled copper crucible of the CELES induction furnace. Ingots of about 100g were obtained and samples for oxidation test were cut, with a parallelepipedic geometry of about 3 x 10 x 10mm³. After a polishing with SiC paper up to 1,200 grid, the samples were exposed to oxidation by air for 50 hours in a tubular furnace, at 1,000°C, 1,100°C or 1,200°C.

Metallographic characterization. After oxidation, an electrolytic nickel layer was deposited on the samples, the oxidized surface of which was become electrically conductive with a first deposition of gold by cathodic evaporation. The samples were cut in two parts using an Accutom-2 saw, which were thereafter embedded in a cold resin (Araldite CY230 + Strengthener Escil HY956). Polishing was performed first with SiC paper from 80 to 1,200 grid under water, and second with a diamond paste 6µm (DP-Suspension P of Struers). The samples were examined using a Scanning Electron Microscope (SEM) Philips XL30, in the Back Scattered Electrons mode (BSE) under an accelerating voltage of 20kV. The thicknesses of the external oxide scales (or of the parts of this scale remaining on surface after cooling), and the depths of the carbide-free zones, were measured in three locations, with calculations of the average value and the standard deviation. Two profiles of concentrations were performed across the zone affected by oxidation, by using a Cameca SX50 microprobe in the Wavelength Dispersion Spectrometry mode, in order to assess the chemical composition changes in this zone and evaluate the chromium depletion.

Results

Chemical compositions and microstructures of the alloys. Table 1 presents the designation and the targeted composition of the nine studied alloys. The two last columns also give a description of the microstructure of the alloys at the intermediate temperature 1,100°C, calculated using Thermo-Calc [4] with a database containing the descriptions of all the M-Cr-C (M=Ni, Co or Fe) systems and their sub-systems. The targeted compositions, which were well respected by the contents really obtained, were used for performing the thermodynamic calculations. These ones showed that the bulk of the nickel-base alloys are constituted of a FCC matrix and Cr₇C₃ carbides (stoichiometry verified by real WDS spot analysis) in the [1,000 – 1,200°C] temperature range. The volume fraction of Cr₇C₃ is about 15% at 1,100°C for the N12 alloy and increases up to almost 25% for the N20 alloy. The matrix of the cobalt alloys is also FCC between 1,000 and 1,200°C, and carbides are also Cr₇C₃ (verified by WDS) with similar volume fractions as the nickel alloys. The microstructure of the iron alloys is more complicated since the nature of the matrix varies with the carbon content.

Table 1. Designations, compositions and microstructures of the studied alloys

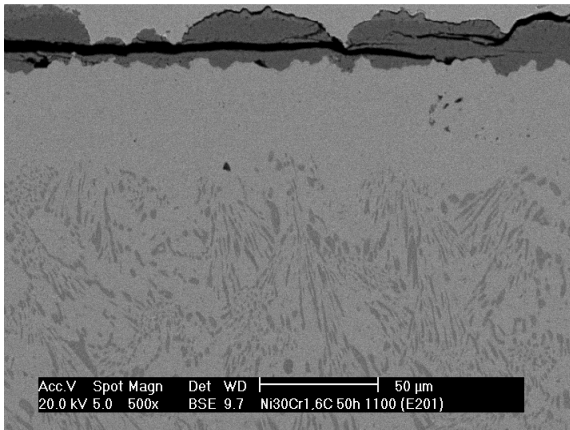
Designation	Targeted chemical composition (% wt.)					Microstructures at 1,100°C (vol. frac. %)	
	Ni	Co	Fe	Cr	C	Cr ₂₃ C ₆	Cr ₇ C ₃
N20	Bal.	/	/	30	2.0	/	24
N16	Bal.	/	/	30	1.6	/	19
N12	Bal.	/	/	30	1.2	/	15
C20	/	Bal.	/	30	2.0	/	23
C16	/	Bal.	/	30	1.6	/	19
C12	/	Bal.	/	30	1.2	/	14
F20	/	/	Bal.	30	2.0	32	/
F16	/	/	Bal.	30	1.6	28	/
F12	/	/	Bal.	30	1.2	21	/

This one is only BCC for F12, both BCC and FCC for F16, and essentially FCC for F20. In addition, the matrix nature also varies a little with temperature, even in the 1,000-1,200°C. These variations of the matrix nature are related to the chromium content in the matrix which depends on the fraction of chromium carbides, i.e. BCC when Cr is more present in matrix and FCC when it is less present because a higher part of this element is involved in the carbides. However, the nature of the present carbides is constant since they are Cr₂₃C₆ in the three iron-base alloys for the three temperatures. Their volume fractions, which are higher than for the Cr₇C₃ in the other alloys, also increases with the carbon content and they can become higher than 30% with the F20 alloy.

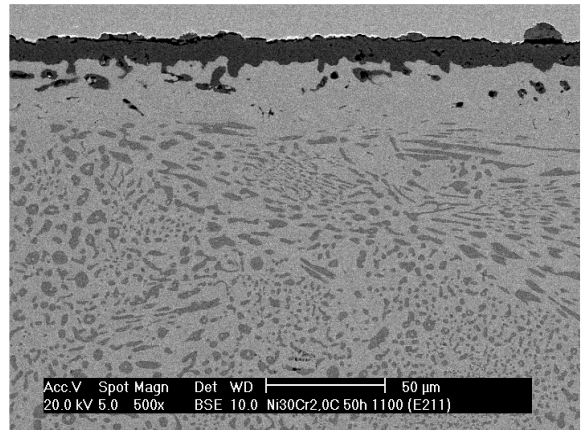
Surface states of the oxidized nickel-base alloys. The oxidized nickel alloys are all covered by an external oxide scale which is essentially chromia (Fig. 1). The thickness of this scale increases with temperature (from about 7µm for 1,000°C up to about 20µm for 1,200°C) but is seemingly not clearly dependent on the carbon content of the alloy. Just under this external scale, an outer zone of the alloy, in which the carbides have disappeared, developed from the external surface. The depth of this carbide-free zone increases with temperature, and also seems to depend on the carbides density. Indeed, it tends to be a little thinner for the N20 and N16 alloys than for N12. In the carbides-richest N20 alloy, in which carbides initially exist with the highest volume fraction and with a homogenous repartition, the carbides seem to be replaced by voids in the carbide-free zone (Fig. 5). One can also notice that there are carbides, in the sub-surface of the N12 alloy oxidized at 1,000 and 1,100°C, which seem to be coarsened in an alloy zone along the inner frontier of the carbide-free zone. This can result to an inwards diffusion of carbon released by the disappearing carbides [5,6]. The depth of the carbide-free zone was measured in three different locations and this led to both average values and standard deviations. They were plotted in the first graph of Fig. 4, in which previous results obtained for a Ni30Cr0.8C alloy oxidized at the same temperatures during the same time are added [7]. This graph illustrates the dependence of the carbide-free zone depth on both temperature and the initial carbides density in the alloy. But there are also some exceptions (e.g. position of the N16 oxidized at 1,100°C).

Surface states of the oxidized cobalt-base alloys. After oxidation, the cobalt alloys are also covered by an external oxide layer (Fig. 2), which is not so homogenous as for the nickel alloys. Both its nature and its thickness evaluate along the external surface. Concerning the nature, as showed by spot WDS microanalysis, some oxides are Cr₂O₃ and others are CoO. The two forms are clearly separated from each other, which can be easily seen since they present two different levels of grey when observed with the SEM in BSE mode (Cr₂O₃ darker than CoO). Like it was earlier observed for Co30Cr alloys containing less carbon (e.g. in [8]), chromia and cobalt oxide can be either superposed (inner CoO and outer Cr₂O₃) or juxtaposed. In addition, oxidation locally penetrates in the alloy (e.g. C20 oxidized at 1,000°C), and in other areas the alloy itself seems to be replaced by oxides (especially for the two highest temperatures). At 1,200°C, there is also a significant attack of the interdendritic spaces in the carbide-free zone. There is other cases for which oxidation can be locally very fast and accompanied by an enhanced interdendritic attack (Fig. 5). Concerning the depth of the carbide-free zone, an increase with temperature is still observed (second graph in Fig. 4). However, on the contrary with what was seen for the nickel-alloys, there is no dependence of the depth of the carbide-free zone on the density of the interdendritic carbides network, even if the results obtained for Co30Cr alloys containing less carbon are added [8]. For the two lowest temperatures, the carbide-free zones of the cobalt-base alloys are seemingly as deep as for the nickel-base alloys, except for the temperature of 1,200°C for which the carbide-free zone is clearly more extended for the cobalt alloys than for the nickel alloys.

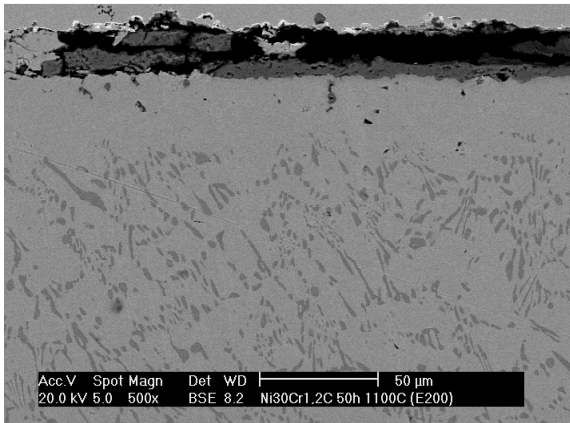
Surface states of the oxidized iron-base alloys. The oxidized iron-base alloys are also covered by an external oxide scale, the thickness of which is generally variable along the extreme surface of the



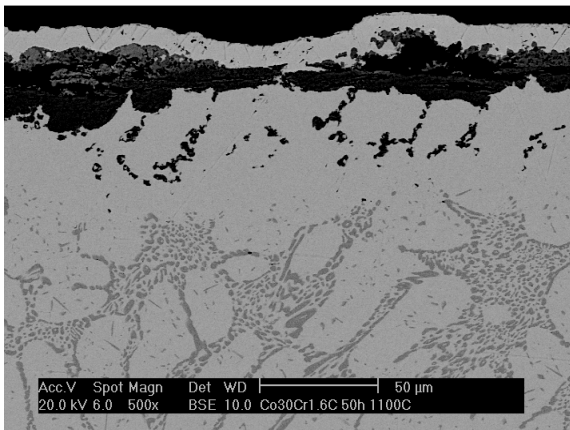
Ni16 after 50h at 1,100°C



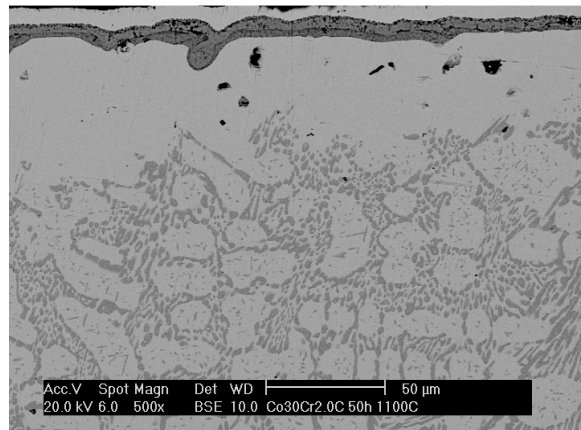
Ni20 after 50h at 1,100°C



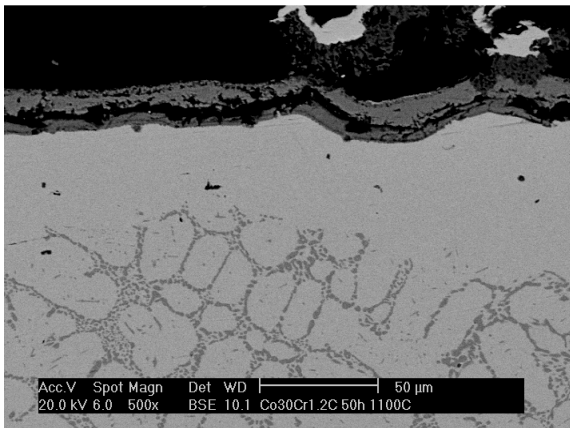
Ni12 after 50h at 1,100°C



C16 after 50h at 1,100°C



C20 after 50h at 1,100°C



C12 after 50h at 1,100°C

Fig. 1.

Surface states of the three Ni-base alloys after oxidation for 50 hours at the intermediate temperature (1,100°C)

Fig. 2.

Surface states of the three Co-base alloys after oxidation for 50 hours at the intermediate temperature (1,100°C)

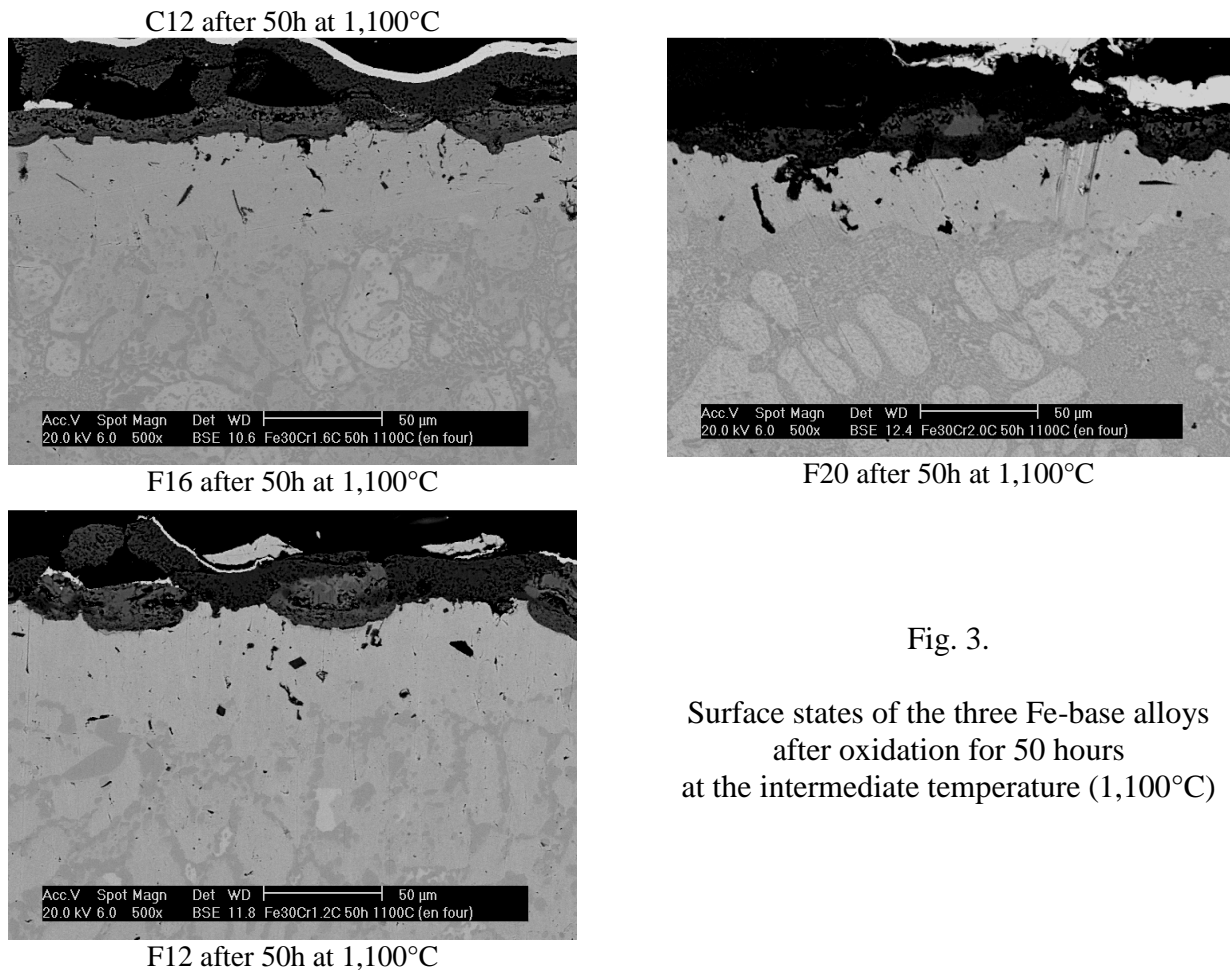


Fig. 3.

Surface states of the three Fe-base alloys after oxidation for 50 hours at the intermediate temperature (1,100°C)

sample. The nature of this oxide also varies, since either two different oxides can be observed separately (superposed or juxtaposed), or a more continuous change of the Cr and Fe contents in the $(\text{Cr,Fe})_2\text{O}_3$ stoichiometry can be revealed across the external scale. A carbide-free zone developed inwards from the extreme surface here too, in which internal oxidation occurred, sometimes especially in the interdendritic spaces. The oxidation front is quite irregular, like for the cobalt alloys and differently to the nickel alloys. The depth of the carbide-free zone always increases with temperature and it is similar to the ones measured for the nickel alloys and for the cobalt alloys for 1,000 and 1,100°C. It is also similar to the nickel-base ones for 1,200°C, i.e. lower than for the cobalt alloys. The difference of carbide-free depth with the 0.8% wt.C-containing alloy studied in [8] is more marked than for the nickel alloys. It also be noticed that the sharing of the matrix of the F16 alloy between the BCC form and the FCC form, which already existed in the whole alloy before oxidation, seems to be modified in the inner part of the zone affected by oxidation. Indeed the pale areas are more frequent and extended than in the bulk (Fig. 5).

Chromium profiles across the zone affected by oxidation. Two chromium content profiles were performed by WDS microanalysis per oxidized sample, across the zone affected by oxidation (including the carbide-free zone, the zone in which carbides have changed when it exists, and in an outer part in the bulk). The results are given in Table 2, in which the average values (calculated with three measures for each sample) of the depth of the carbide-free zone is reminded for comparison.

Of course all samples display a chromium depletion from the external surface, which is more or less extended, this depending on the base element, the carbides fraction and the temperature). In most cases, the zone of Cr-depletion obviously corresponds to the carbide-free zone. But it is true that the depletion depth is also often more extended than the carbide-free zone. For the chromium

depletion, one finds again the same phenomenon as already met above for the carbide-free depth: the chromium depletion depth increases when the temperature raises and when the carbon content or the carbide fraction decreases.

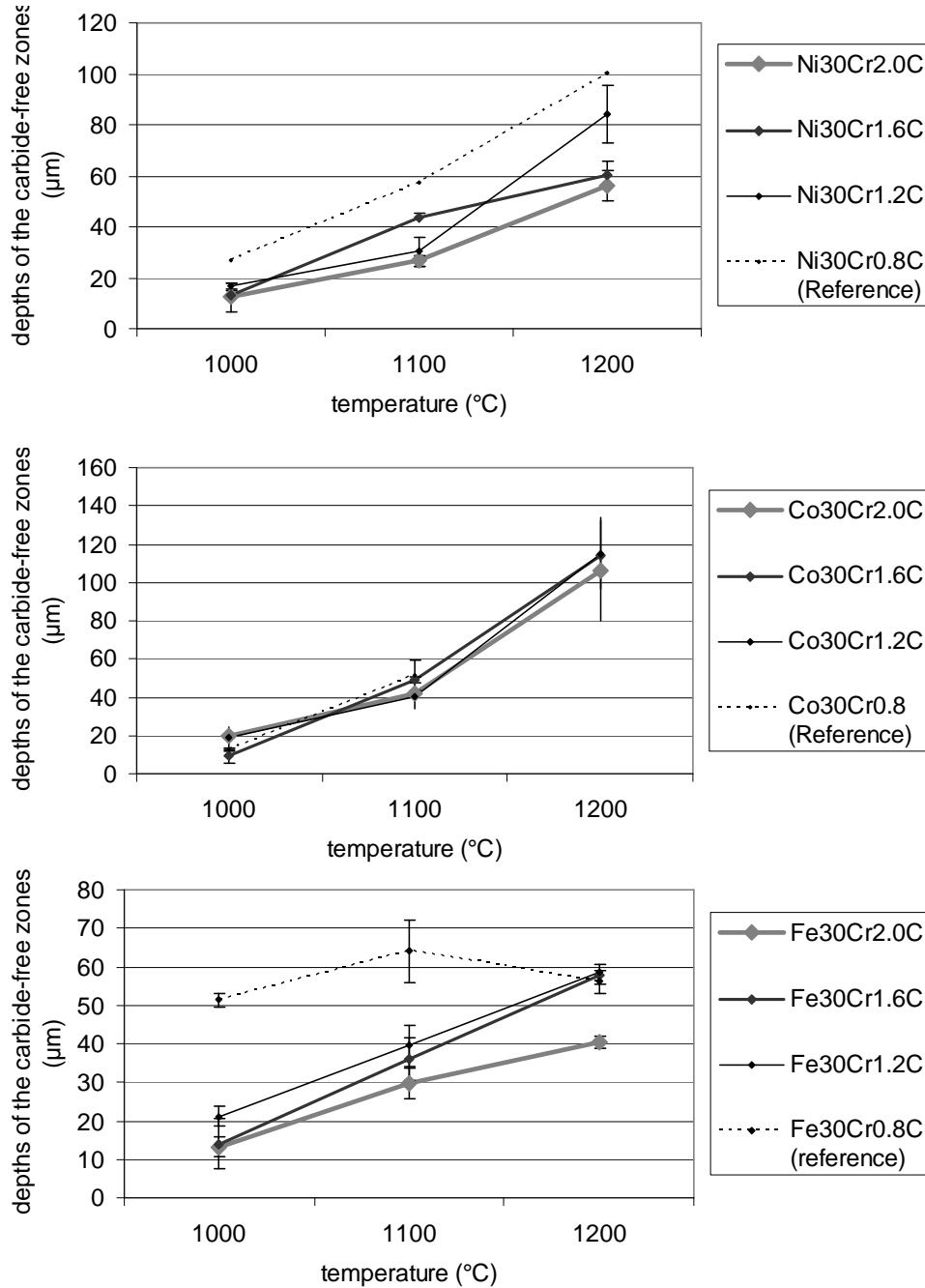


Fig. 4. Evolution of the depth of the carbide-free zone with the carbon content and the temperature for the Ni-base (top), Co-base (middle) and Fe-base (bottom) alloys

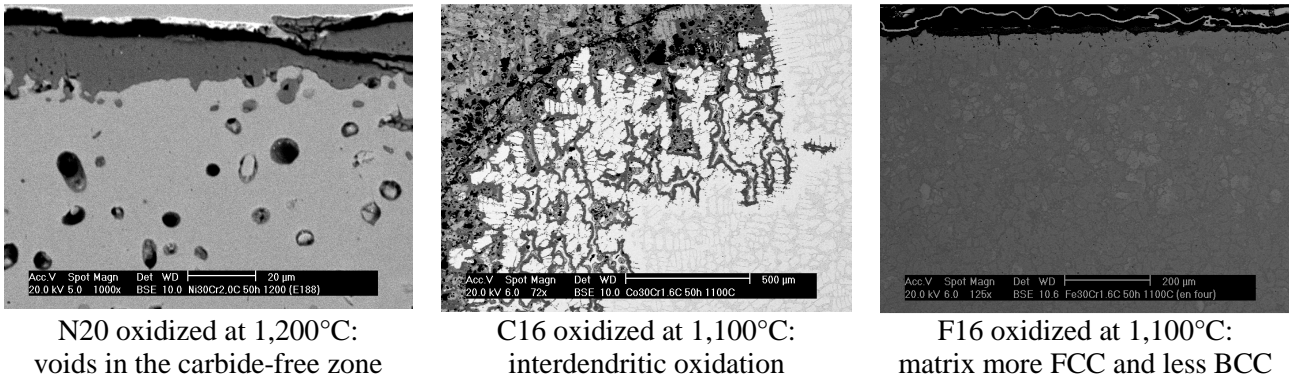


Fig. 5. Several special local consequences of high temperature oxidation in the sub-surface of some Ni-base (left), Co-base (middle) and Fe-base (right) alloys

Table 2 also presents the values of the average Cr content in the extreme surface for all samples. Generally these Cr contents on surface are higher for the nickel alloys than for the cobalt alloys, and for the latter than for the iron alloys. This Cr content on surface also decreases when the carbides fraction increases, and finally the Cr content on surface increases with temperature. The average values of the Cr gradient across the zone affected by oxidation are also given. All Cr gradients decrease when the temperature increases, and they are generally lower for the nickel alloys than for the cobalt alloys, and lower for the latter than for the iron alloys. Their dependence on the carbide fraction is clear in the case of the nickel alloys and the cobalt alloys since the gradient decreases when the carbide fraction increases, at all temperatures (but there are one or two exceptions). It is more complicated in the case of the iron alloys for which it was sometimes impossible to define a gradient.

Discussion

These (Ni, Co or Fe)-30Cr-1.2 to 2.0C alloys containing very high carbides fractions all displayed a high temperature oxidation behaviour which appeared to be never catastrophic during 50 hours at temperatures which were very high, although they contain high atomic contents of carbon. Initially one can think that this element either will induce itself a catastrophic behaviour, because of its oxidation into gaseous species, or will promote a loss of the chromia-forming behaviour of the emerging matrix. Concerning this second point, the chromium content in matrix was effectively very lowered by the precipitation of high fractions of chromium carbides in grain boundaries. In fact, the chromia-forming behaviour of the nickel alloys was kept, even when the temperature was as high as 1,200°C, while the cobalt alloys and the iron alloys, which are not really Cr₂O₃-forming at these temperatures when they contain less carbon [8], did not really change of behaviour. Indeed, the formation, on the external surface, of Cr₂O₃ and CoO together, or of (Cr,Fe)₂O₃, was already encountered respectively for Co - 30Cr - 0 to 0.8%C alloys and Fe - 30Cr - 0 to 0.8%C alloys, in a previous work [8]. Here too, oxidation penetrated inwards the (cobalt or iron) alloy with an irregular front, since first the whole alloy began to be attacked, and second oxidation locally accelerated in several points of the oxidation front.

In all cases a carbide-free zone developed from the external surface because of the participation to the oxidation on the external surface, of the chromium contained in the carbides, together with chromium present in solid solution in matrix. For a same carbon content, the carbide-free zone is less extended for the iron alloys than for the nickel alloys, probably because the penetration of the oxidation front into the iron alloys since both Cr and Fe are obviously oxidized together. About the cobalt alloys, for which cobalt is also oxidized in the same time as chromium, the very deep

Table 2. Comparison between the average values of the carbide-free depths and of the Cr-depleted depths (WDS microanalysis); average values of the Cr-content in extreme surface and of the Cr weight content gradient

Alloy	1,000°C during 50 hours		1,100°C during 50 hours		1,200°C during 50 hours	
	carb.-free d. (µm)	Cr deplet. (µm)	carb.-free d. (µm)	Cr deplet. (µm)	carb.-free d. (µm)	Cr deplet. (µm)
N20	12	30	27	30	56	30
N16	13	15	44	50	61	50
N12	17	25	30	30	84	70
C20	20	20	42	40	106	100
C16	9	25	49	40	114	100
C12	19	25	40	75	115	200
F20	13	10	30	35	40	?
F16	14	20	36	60	58	70
F12	21	20	40	50	59	90

Alloy	1,000°C during 50 hours		1,100°C during 50 hours		1,200°C during 50 hours	
	minimal %wt. Cr	Cr gradient (%wt./µm)	minimal % wt. Cr	Cr gradient (%wt./µm)	minimal % wt. Cr	Cr gradient (%wt./µm)
N20	14	0.058	14	0.019	18	0.016
N16	17	0.069	16	0.060	18	0.012
N12	18	0.164	20	0.057	20	0.021
C20	13	0.234	7	0.351	16	0.047
C16	12	0.461	15	0.138	16	0.062
C12	18	0.525	10	0.180	17	0.074
F20	13	?	10	0.518	?	?
F16	11	0.727	11	0.251	18	0.057
F12	15	0.368	11	0.238	15	0.100

carbide-less zone in some cases are probably related to a higher rate of oxidation than for nickel alloys. This was not easy to verify on the *post mortem* samples since oxides partly quitted the samples during cooling and the quantity of oxides observed by metallography was then minimized.

Chromium diffuses both along grain boundaries and through the matrix. The second phenomenon is more or less easy, this depending on the temperature, the nature of the matrix (chromium gradients in nickel matrix lower than in cobalt or iron matrixes) and, seemingly, with the density of the carbides network. Indeed, the Cr gradient appeared to be lowered by an increased carbon content. One can also notice the matrix change of the 1.6%wt.C-containing iron alloy, which is probably due to the small impoverishment of chromium in the inner part of the zone affected by oxidation. In this zone of this alloy, the carbon content of which led to an intermediate Cr content in matrix allowing the presence of the BCC and FCC forms simultaneously, a part of BCC (favoured by Cr) appeared to be effectively converted in FCC.

Conclusion

Even when they content high fraction of carbides, e.g. for achieving special mechanical properties, the Ni-30Cr based alloys, but also the Co-30Cr and Fe-30Cr based alloys, are able to resist oxidation at least for several tenths hours at high temperature. But such alloys are especially

exposed to catastrophic oxidation (which never occurred here) because of the great carbon content and of the low Cr contents in matrix due to the precipitation of high fraction of chromium carbides.

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