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Metallography study of the surface states of alloys heated at very high temperatures in oxidizing conditions

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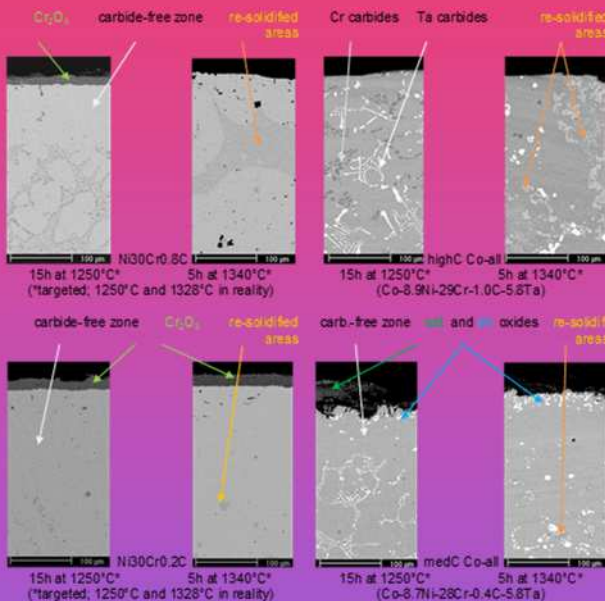
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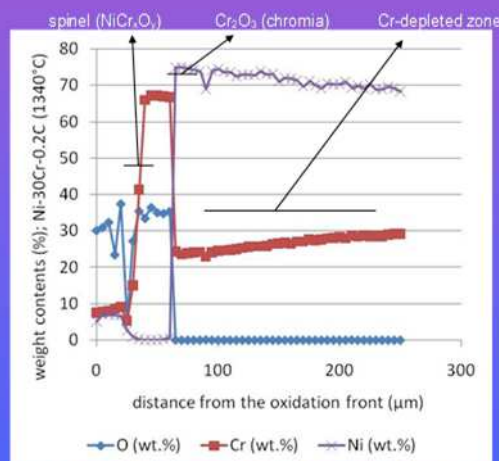
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In service, the refractory alloys used in the hottest parts of industrial machines may accidentally encounter extremely high temperatures, which even can reach their solidus temperature. If these very high temperatures are only several tens Celsius degrees below the alloy solidus temperature several hours can be enough to significantly modify the microstructure of the alloy as well as its chemical composition in sub-surface, and then the resistance of the alloy against hot oxidation. If this temperature is slightly higher than the fusion start temperature of the alloy, this one can be partially molten and some liquid zones can be more or less exposed to oxidation, in some cases separated from the oxidizing gases by a thin layer of alloy or directly exposed to these gases. Such conditions may lead to fast catastrophic oxidation inward the bulk. The purpose of this work is to specify the surface state of several alloys in order to assess their remaining potential of resistance against hot oxidation.



Surface states of selected samples (SEM in BSE mode)

(Only the Ni-based alloys were thereafter characterized by WDS profiles and metallographic measurements)



Example of WDS profile, with identification of the nature of external oxide (here chromia with a spinel oxide on its outer surface) and evidencing the depth of alloy depleted in chromium

Typical thicknesses of the chromia scales on the surface of the nickel-based samples after oxidation

thickness of the external Cr ₂ O ₃	Ni-30Cr-0.2C	Ni-30Cr-0.4C	Ni-30Cr-0.8C
after 5h at 1328°C	18.2±0.9 μm (extr. to 15h: 30.0 – 33.1)	14.6±3.9 μm (extr. to 15h: 18.5 – 22.0)	No oxide remains on surface
after 5h at 1316°C	8.3±2.4 μm (extr. to 15h: 10.2 – 18.5)	15.1±2.4 μm (extr. to 15h: 22.0 – 30.3)	15.6±1.6 μm (extr. to 15h: 24.2 – 29.8)
after 15h at 1300°C	14.6±2.4 μm	23.4±1.6 μm	21.4±2.4 μm
after 15h at 1250°C	18.8±2.7 μm	17.7±3.9 μm	14.1±1.6 μm

*extr. = extrapolated to 15h assuming a parabolic rate (i.e. square root of time)

Intervals including the 4 values measured by WDS microanalysis for the minimal chromium content obtained on extreme surface

Chromium content on extreme surface	Ni-30Cr-0.2C	Ni-30Cr-0.4C	Ni-30Cr-0.8C
after 5h at 1328°C	23.3-24.4 wt.%Cr	22.3-23.6 wt.%Cr	26.4 wt.%Cr
after 5h at 1316°C	23.3-24.1 wt.%Cr	21.1-26.7 wt.%Cr	22.1-25.9 wt.%Cr
after 15h at 1300°C	20.8-22.3 wt.%Cr	19.7-20.5 wt.%Cr	20.9-21.8 wt.%Cr
after 15h at 1250°C	23.5-24.6 wt.%Cr	20.7-23.8 wt.%Cr	23.2-23.9 wt.%Cr

Comparison between the interval of depletion in Cr revealed by 2 WDS profiles per sample and the carbide-free depth (average value ± std deviation out of 3 values)

depth of Cr depletion	Ni-30Cr-0.2C	Ni-30Cr-0.4C	Ni-30Cr-0.8C
carbide-free zone (or outer alloy zone without molten areas in the case of 1328°C)			
after 5h at 1328°C	180-200 μm	100-170 μm	130 μm
	169±6 μm	132±8 μm	83±9 μm
after 5h at 1316°C	150-160 μm	90-120 μm	90-160 μm
	226±8 μm	170±8 μm	109±6 μm
after 15h at 1300°C	150-160 μm	130-140 μm	80-90 μm
	183±18 μm	119±11 μm	80±7 μm
after 15h at 1250°C	230-260 μm	200-230 μm	110-150 μm
	161±7 μm	171±25 μm	/

Total mass of chromium lost by the depleted zone (per cm² of external surface) because of outwards diffusion and oxidation (two values resulting from integration over 2 WDS profiles, except*)

Chromium content on extreme surface	Ni-30Cr-0.2C	Ni-30Cr-0.4C	Ni-30Cr-0.8C
after 5h at 1328°C	5.7-5.8 mg/cm ² (extr. to 15h: 9.9 – 10.0)	5.3-7.8 mg/cm ² (extr. to 15h: 9.2 – 13.5)	4.7-5.5 mg/cm ² (extr. to 15h: 8.1 – 9.5)
after 5h at 1316°C	3.4-3.8 mg/cm ² (extr. to 15h: 5.9 – 6.6)	6.8-8.5 mg/cm ² (extr. to 15h: 11.8 – 14.7)	5.1-7.5 mg/cm ² (extr. to 15h: 8.8 – 13.0)
after 15h at 1300°C	8.1-9.4 mg/cm ²	8.1-9.3 mg/cm ²	4.5-6.9 mg/cm ²
after 15h at 1250°C	6.7-7.7 mg/cm ²	8.1-11.6 mg/cm ²	6.9 mg/cm ²

The three Ni alloys and the two Co-based superalloys correctly resisted to oxidation at these four very high temperatures, even if they are partially molten. This can be attributed first to the initial high Cr content in all the alloys (28 to 30wt.%) and also, in the case of 1328°C for which all alloys were partially molten, to the single-phase zone formed by oxidation at heating which prevents thereafter any contact between the oxidizing gases and these molten areas, and then possible catastrophic oxidation. The minimal chromium contents on extreme surface let think that the resistance of the alloys against hot oxidation may go on several supplementary hours.