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# Influences of the Base Element, the Oxide Scale Thickness and the Cooling Start Temperature on the Oxide Spallation of Cast Alloys during the Post-Isothermal Oxidation Cooling

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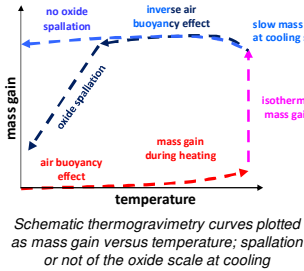
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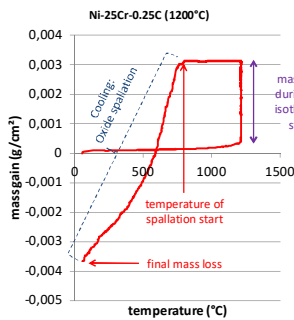
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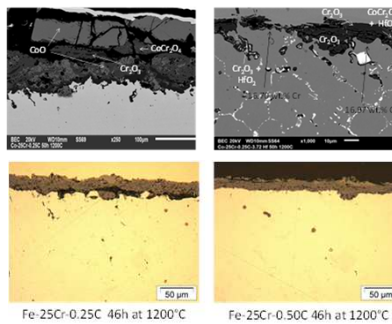
After the isothermal oxidation rate, one of the most important properties characterizing the high temperature oxidation resistance of refractory metallic alloys [1,2] is the resistance of the formed protective oxide scale against spallation during thermal variations. Indeed, repeated oxide spallation during thermal cycling accelerates the impoverishment of the alloy's sub-surface in aluminum or chromium. The well-known parameters influencing this phenomenon are the ratio between the average thermal expansion coefficients of the oxide and of the alloy, the cooling rate and the chemical composition of the alloy (notably the presence in small quantities of active elements or compounds as hafnium or yttrium). Other parameters are maybe to be also taken into consideration, as the thickness of the oxide just before cooling and the level of temperature range in the first part of the cooling. To study the effect of these two other parameters, numerous model cast alloys based on cobalt, nickel or iron, rich in chromium (25 wt.%) and containing carbides of different natures (chromium carbides, HfC...) and in various fractions (carbon contents varying between 0.25 to 0.50wt.%), were subjected to oxidation in dry synthetic air at different temperatures (1000, 1100 and 1200°C) and for different durations (46 or 50h), using a thermo-balance. For a same cooling rate (-5 °C/min), the mass variation curves recorded during the cooling were, after correction from the air buoyancy variations, plotted versus temperature instead time. Several parameters characterizing the oxide spallation were noted (temperature of spallation start, average rate of mass loss and final mass loss [3 to 6]) and the noticed differences interpreted.



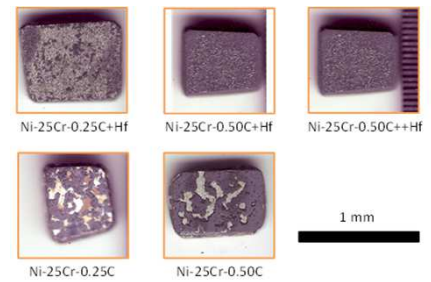
Schematic thermogravimetry curves plotted as mass gain versus temperature; spallation or not of the oxide scale at cooling



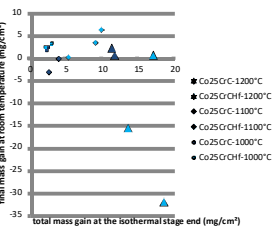
Real thermogravimetry curves plotted as mass gain versus temperature; parameters characterizing the spallation of the oxide scale



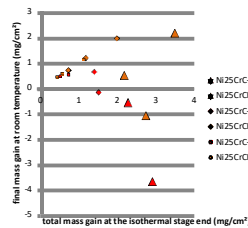
Different natures and thicknesses of the external oxide scales resulting from different base elements and general chemical compositions of the alloys, and from different temperatures and durations of oxidation



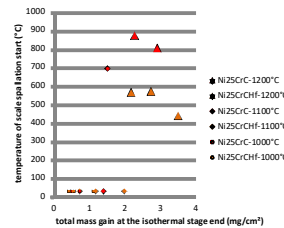
Different degrees of oxide scale spallation during cooling at a given rate



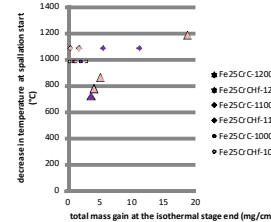
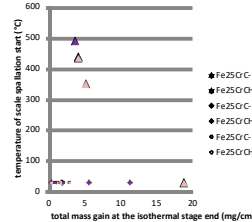
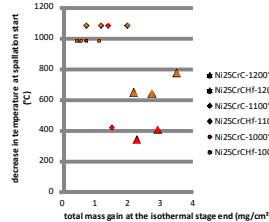
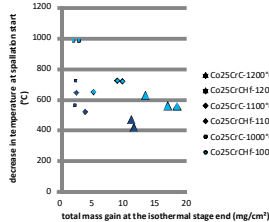
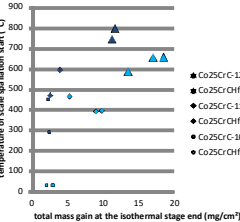
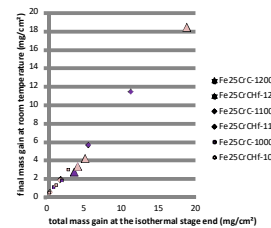
Cobalt-based alloys (25Cr, 0.25 or 0.50C, 3.7 or 7.4Hf, in wt.%)



Nickel-based alloys (25Cr, 0.25 or 0.50C, 3.7 or 5.6Hf, in wt.%)



Iron-based alloys (25Cr, 0.25 or 0.50C, 3.7 or 5.6Hf, in wt.%)



In this study it first appeared that, for such {M-25wt.%Cr}-based cast alloys, that the base element is of importance since – beside its possible mismatch of thermal expansion behaviour with the external oxide – it strongly influences the nature of the scale: mainly chromia for Ni alloys, presence of additional CoO and CoCr<sub>2</sub>O<sub>4</sub> for Co alloys, (Fe,Cr)<sub>2</sub>O<sub>3</sub> for Fe alloys... But another important parameter is the quantity of oxide formed (during heating + mainly isothermally), which increases with the temperature stage but also with the complex nature of the oxides formed (thicker scales if presence of CoO and CoCr<sub>2</sub>O<sub>4</sub> oxides resulting of the faster oxidation of the Co-based alloys). The presence of hafnium, here in great quantities for promoting the formation of HfC carbides, played its usually beneficial role for the resistance against spallation.

Among the alloys studied here, the best resistant against oxide scales spallation were the iron-based alloys (none loosed parts of their scales during cooling). The nickel-based were themselves rather resistant against this phenomenon, except after oxidation at the highest temperature 1200°C which led to too thick scales to allow them to do not suffer spallation. The worst alloys of this study are the cobalt alloys. These ones, not rich enough in chromium to be really have a chromia-forming behaviour, were often covered by a very thick multi-composed oxides scales, which led to early spallation start and severe mass losses.

## References

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