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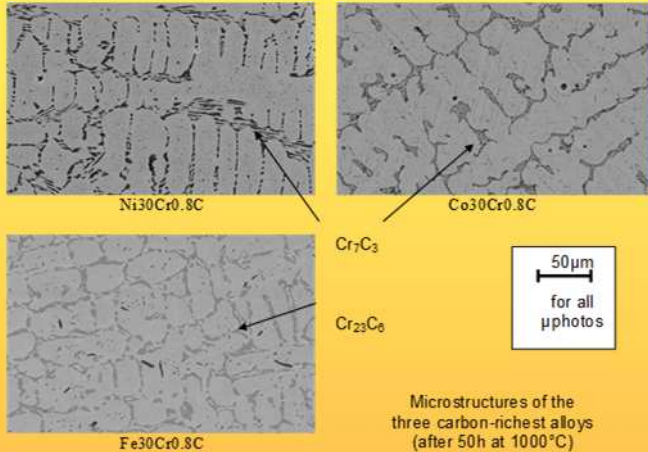


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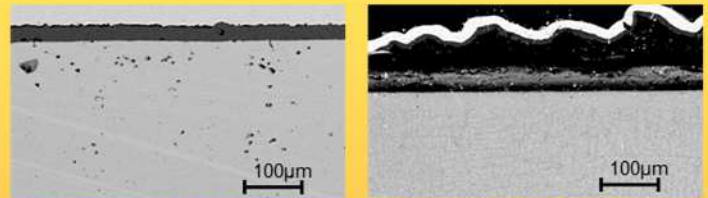
Correlation between the external oxide scale adherence and the bulk's thermal expansion behaviour for several carbides strengthened refractory alloys

Patrice BERTHOD

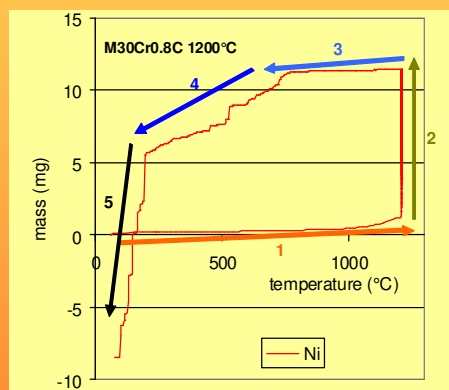
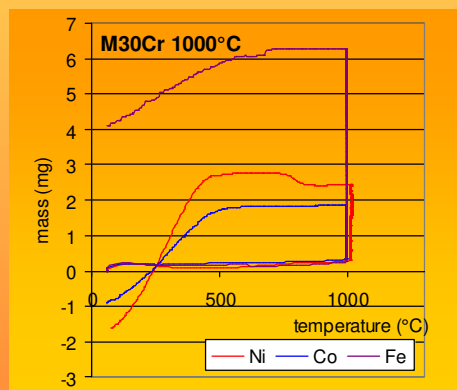
During thermal cycles at high temperature the alloys are currently affected by a partial or total loss of the oxide scale formed before on their external surface. This loss of the protective oxide layer, which accelerates the degradation of most alloys during their use in practical conditions, is logically attributed to the thermal contraction during cooling. The thermal expansion or contraction phenomenon can depend on the microstructure of the alloy, notably on the nature of its matrix and on its carbide volume fraction. The aim of the present study is to characterize the progress of the spallation during cooling by exploiting the cooling parts of thermogravimetry curves, in the case of cast alloys belonging to different families (chromiumrich Cobased, Ni-based and Febased alloys, with or without interdendritic carbides) and to try to correlate this with their thermal expansion behaviours.



Six alloys (Ni, Co or Fe)30wt.%Cr with 0 or 0.8 wt.%C were synthesized by high frequency induction melting. They were oxidized at three different temperatures (1000, 1100 and 1200°C, heating rate of 20 K min⁻¹, isothermal stage during 50 hours and cooling at 10 K min⁻¹) with thermogravimetry measurement and SEM examination of their oxidized surfaces. The thermal expansion behaviours of these alloys were also studied by dilatometry.



Oxidized surfaces of two of the thermogravimetry samples



Plot of mass gain versus temperature (here M30Cr0.8C at 1200°C):

- heating (decreasing Archimede pressure and first mass gain, 1),
- dwell at 1200°C (isothermal mass gain, 2),
- beginning of cooling (no spallation, 3),
- cooling (spallation, 4) and
- cooling end (additional spallation, 5)

Temperatures of transition between two successive mass loss rates

Alloys	dwell at 1000°C	dwell at 1100°C	dwell at 1200°C
Ni30Cr	↑ at 810°C 450±30°C (3→4)	710±10°C (3→4) 290±60°C (4→5)	880±10°C (3→4) 620±10°C (4→5)
Ni30Cr0.8C	↑ at 940°C 690±20°C (3→4)	590±90°C (3→4)	770±70°C (3→4) 200±0°C (4→5)
Co30Cr	500±70°C (3→4)	370±40°C (3→4) 210±20°C (4→5)	600±40°C (3→4) 410±20°C (4→5)
Co30Cr0.8C	↑ at 800°C 170±100°C (3→4)	320±20°C (3→4) 70±5°C (4→5)	↑ at 800°C 160±100°C (3→4)
Fe30Cr	600±60°C (3→4)	470±40°C (3→4)	370±30°C (3→4)
Fe30Cr0.8C	400±70°C (3→4)	340±20°C (3→4)	420±30°C (3→4)

The first fast decrease in mass (3→4) occurs at an average temperature which is higher for the Ni alloys (825°C) than for the Co alloys (average 600°C), and for the latter higher than for the Fe alloys (395°C), during cooling after 50h at 1200°C. This order almost remains for 1100°C since the (3→4) transition takes place at 650°C, 345°C and 405°C for respectively the Ni, Co and Fe alloys. For 1000°C such comparisons are not possible since the jump phenomenon affects most of the alloys.

The same hierarchy seems existing for the second acceleration of decrease in mass (4→5), when it exist, since the transition temperature is also lower for the Co alloys than for the Ni alloys, while this second acceleration does not occur for the Fe alloys (does this mean that the (4→5) temperature should be lower than room temperature?).

This can be easily explained by the difference of thermal expansion coefficient between external oxide and alloy which is higher for the Ni alloys and Co alloys (18 to 21×10^6 K⁻¹), than for Fe alloys (15 to 17×10^6 K⁻¹). The difference between the Ni alloys and the Co alloys may result from an external oxide which is essentially Cr₂O₃ (7.3×10^6 K⁻¹) on Ni alloys' surfaces while it is often a mix of Cr₂O₃ and CoO (15.0×10^6 K⁻¹) on Co alloys' surfaces. The jump sometimes seen at 1000°C is an accommodation of compressive stresses increasing in the external oxide during cooling, by locally bowing the scale which allows the denuded alloy oxidizing quickly again.

Despite their low efficiency because of variation of the apparent weight of the oxidized samples due to decreasing temperature, the last part of the thermogravimetry measurements can be of great interest for specifying, not really the mass of lost oxide during cooling, but temperatures at which these losses occurred. For example this allows knowing if the loss of external oxide which can be observed on sample at room temperature acted abruptly at a given temperature or on the contrary was diluted along a temperature range which can be also determined. Here this allowed, for example, seeing that the external oxide covering nickel or cobalt alloys was lost after less cooling than for iron alloys which exhibit lower coefficients of thermal expansion, i.e. less far from the oxides ones.