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Characteristics and resistance against spallation of the oxides formed at high temperature on {Co, Ni}–based chromium–rich cast alloys containing titanium

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Introduction & Experimental

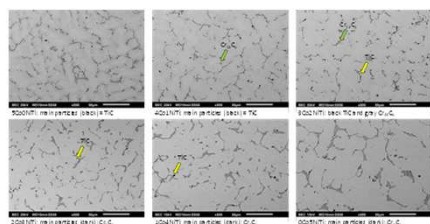
Titanium is a MC carbide-forming element which can be used to obtain carbides, in addition to other carbides or as single carbide present. These carbides are able to take part to the interdendritic mechanical reinforcement for resisting stresses at high temperature. However, titanium can strongly react with oxygen or nitrogen. Consequently its presence may influence the general behavior of chromia-forming alloys in oxidation at high temperature, by promoting the formation of other oxides than chromia.

In this work, a series of samples all containing 25 wt.%Cr, 0.4wt.% C and 1.6wt.%Ti, with a base element shared between nickel and cobalt in various proportions, were exposed at 1250°C during 70 hours with mass gain recording. The variation of mass during a -5°C min⁻¹ cooling was monitored also using the thermo-balance and the oxidized states and deteriorated sub-surfaces after return to room temperature were characterized.

Results / Compositions and microstructures of the alloys

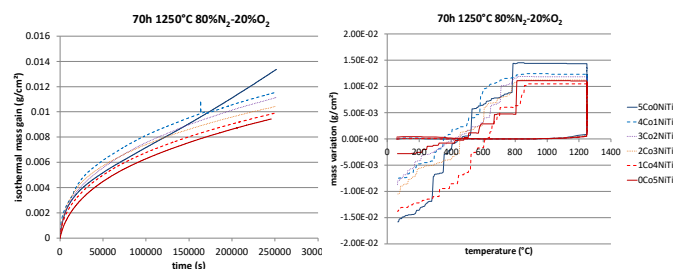
- Ni/Co ratios distributed between 0 (Ni-free cobalt-based) and 1 (Co-free nickel-based)
- Microstructures typical of conventionally cast alloys: dendritic matrix, eutectic carbides
- Ni-free cobalt-based alloy: titanium carbides only; Co-free nickel-based alloy: chromium carbides only; simultaneous presence of Co and Ni: co-existence of both types of carbides

wt.%	M (*:Co, **:Ni)	Cr	Ti	C
0Co5NiTi	0*	25	1.6	0.4
1Co4NiTi	15*	25	1.6	0.4
2Co3NiTi	29*	25	1.6	0.4
3Co2NiTi	29**	25	1.6	0.4
4Co1NiTi	15**	25	1.6	0.4
5Co0NiTi	0**	25	1.6	0.4



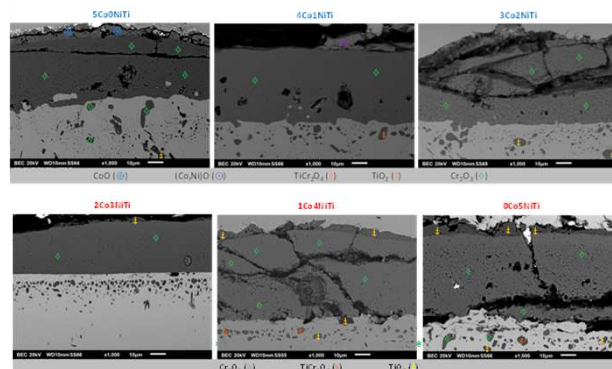
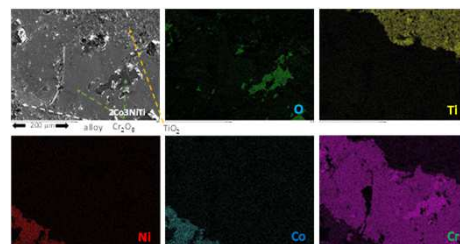
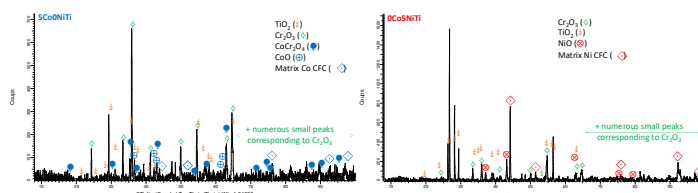
Results / Mass variation phenomena and kinetics: isothermal stage and cooling

- Isothermal: all curves similar to parabolas; tendency to faster kinetic for the cobalt–richest alloys than for the nickel–richest ones
- Isothermal: regime tipping from parabolic to linear in the case of the Ni-free cobalt-based alloy near the middle of the test
- Rather severe oxide scale spallation during the post-isothermal stage cooling; no clear dependence, on the Ni/Co ratio, of the spallation start temperature and of the final mass loss achieved at the test end



Results / Post-mortem characterization of the oxidized surface: XRD, EDS elemental images, cross-sectional SEM

- Many denuded alloy areas (spallation at cooling, handling)
- External scales mainly made of chromia
- Presence of an outermost oxide layer CoO, (Co,Ni)O for the Co-richest alloys or NiO for the Ni-richest ones, TiO₂ notably for the Ni-richest alloys



Summary / Conclusions

- The nature of the interdendritic carbide network precipitating at the end of solidification is dependent on the base element: Co favors TiC and Ni favors chromium carbides.
- Over 70 hours at 1250°C the global oxidation rate is influenced neither by the base element, nor by the form with which titanium is present in the alloy (as TiC carbides or as solute in the matrix); however, catastrophic oxidation threatens the cobalt-richest alloy earlier than the other alloys.
- Thank to the 25 wt.%Cr contained by the alloys, all of them are chromia-forming, at least up to 50 hours.
- Titanium is involved in internal oxidation but an outermost TiO₂ layer formed at the top of the chromia scale, particularly in the case of the nickel-richest alloys (phenomenon related to a higher mobility of Ti when not trapped in TiC carbides?)
- Does the outermost TiO₂ layer protect the chromia scale against volatilization?

