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A systematic study of the effect of the nickel and cobalt respective proportions in M-30Cr alloys (M = Ni and/or Co) on their behavior in oxidation at high temperature

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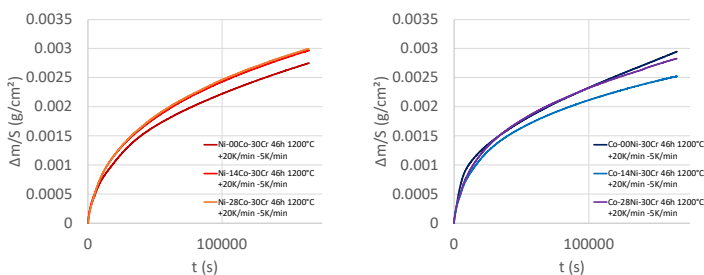
Introduction & Experimental

Nickel and cobalt are frequently present together in cast superalloys. For instance nickel is almost systematically present in the chemical composition of cobalt alloys to help the austenitic structure to remain stable despite the temperature variations which may occur in service. It is often observed that the oxidation behavior at high temperature is better in great presence of nickel than in great presence of cobalt. The aim of this study is to explore the effect of the Co/Ni ratio on the oxidation behavior in the case of simple cast alloys composed of nickel, cobalt and chromium only, and elaborated following exactly the same procedure. Thermogravimetric tests were carried out in air at 1200°C, followed by post-mortem characterization of the oxidized samples (XRD, SEM, EDS).

A series of six $\{(70-x)\text{Co}-x\text{Ni}-30\text{Cr}; 0 \leq x \leq 70\}$ alloys were elaborated by conventional foundry. First, the obtained general chemical compositions were controlled by energy dispersive spectrometry. Second, thermogravimetric tests at 1200°C were performed, followed by the exploitation of the mass gain files to access to the oxidation kinetics. Post-mortem characterization was carried out for knowing the natures and quantities of the oxides formed and the subsurface changes induced by oxidation.

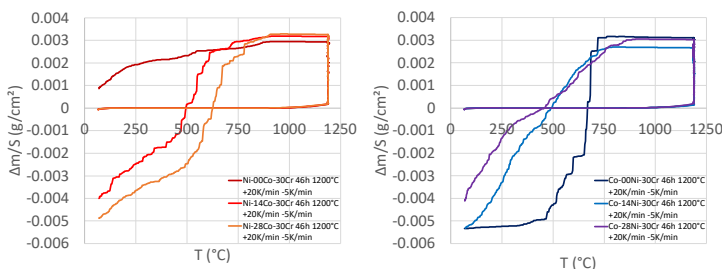
Results / Mass gain and mass loss phenomena and their kinetics: isothermal

- Kinetics globally all parabolic
- Curiously for these model alloys, no significant difference between the nickel-richest alloys and the cobalt-richest alloys
- Parabolic constants K_p (corrected from chromia volatilization) for all alloys: all about 30 to 50 $\times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ (compatible with chromia growth at this temperature in air)
- Chromia volatilization constants K_v (chromia volatilization) for all alloys: all about 30 to 100 $\times 10^{-10} \text{ g cm}^{-2} \text{ s}^{-1}$ (remaining typical of this temperature in air)



Results / Mass variation phenomena and kinetics: cooling

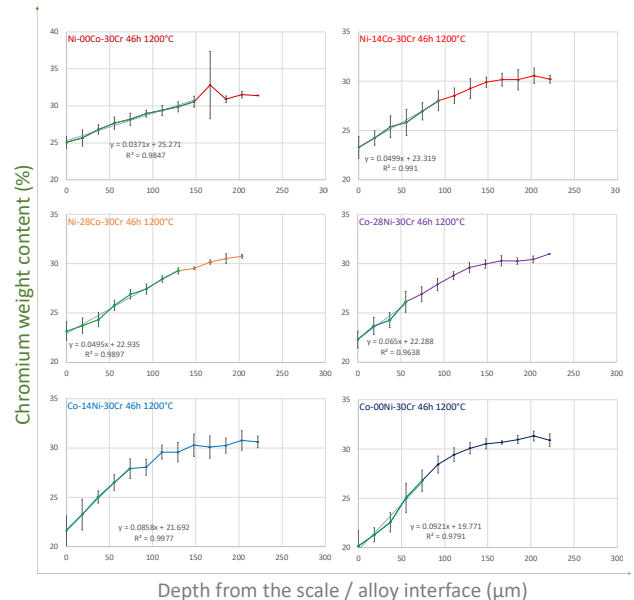
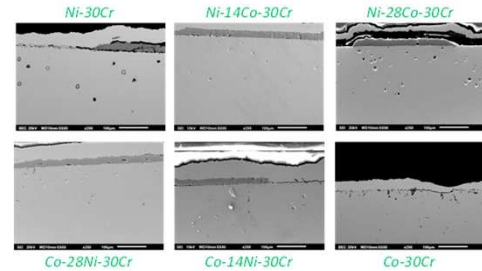
- Early starts of oxide scales spallation during cooling: about 900°C for all alloys (i.e. after only 300°C of cooling) except for the two cobalt-richest alloys which start spalling off a little later (when $T \approx 750^\circ\text{C}$)
- Except one (Ni-30Cr), negative values for total mass changes along the whole thermal cycle



Results / Post-mortem characterization

- Surface: only small parts of external oxide (Cr_2O_3) to examine and characterize (spallation)
- Sub-surface: the chromium content in subsurface close to the interface with the external oxide scale regularly decreases from 25 wt.% to 20 wt.% Cr when Ni is progressively replaced by Co; at the same time the chromium gradient increases from 40 to 90 wt.%Cr / mm; the Cr-depleted depth tends decreasing but stays in the 150–200 μm range

Oxidation states after 46h of oxidation at 1200°C in synthetic air



Summary / Conclusions

- In fact, in the case of these binary and ternary alloys, the mass gain kinetics as well as the oxide spallation at cooling remain all rather similar to one another, although the maximal amplitude of the (Ni by Co) replacement; obviously, if they really exist, the differences between the cobalt-based alloys and the nickel-based alloys stay inconspicuous during the four first tens of hours in air at 1200°C.
- In contrast, significant differences are evidenced by the Cr concentration profiles: when more and more cobalt comes substituting nickel, the minimal Cr content decreases and becomes closer and closer to critical values, while the %Cr gradient value increases; for similar final mass gain rates this means that the diffusion coefficient decreases with the Co addition.
- Much more visible differences are expected for longer times, since the Co-richest alloys will certainly fall soon in a catastrophic oxidation while the Ni-richest can stay chromia-forming.

