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Oxidized states of chromium–rich {Co,Ni}–based alloys rich in tantalum to form TaC carbides after exposure at 1250°C in air

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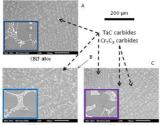
Introduction & Experimental

Tantalum carbides are among the most stable MC primary carbides in the cast superalloys when they are exposed at elevated temperature. When chromium is present in the chemical composition for achieving high resistance against hot oxidation and hot corrosion, the TaC carbides are particularly present in cobalt-based superalloys, but less in the nickel-based ones for equivalent contents in tantalum and carbon. In all cases a part of the tantalum atoms stays in solid solution in the matrix and Ta atoms are able to diffuse toward the oxidation front. The purpose of this work is to examine, after exposure at a temperature high enough to facilitate the dissociation of TaC carbides and a fast diffusion of the Ta atoms, how tantalum behaved and where it went, in the case of {Co,Ni}-based alloys containing the same contents in Cr, C and Ta.

Three alloys, all containing 25Cr, 0.4C and 6Ta, called CBLT (Co- 0Ni), CBLT+Ni (Co-13Ni) and CBLT++Ni (Co-26Ni), all contents in wt.%, were elaborated by conventional foundry. After having checked that their melting start temperatures allow that, they were subjected to thermogravimetric tests at 1250°C for 70 hours in air. The exploitation of the mass gain files, plotted versus time but also versus temperature, and post-mortem characterization for examining the surface and subsurface degradation induced by oxidation, were carried out.

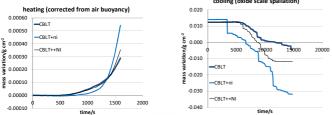
Results / Preliminary checking of the obtained alloys: microstructures and refractoriness

- Typical solidification microstructures: dendrites of austenitic matrix, eutectic carbides
 Carbides exclusively TaC in all cases; script–like morphology favorable for high creep resistance at elevated temperature
- Solidus temperatures (1320 1340°C) high enough to allow tests at 1250°C without melting
 Liquidus temperature (1415 1425°C) low enough for allowing rather easy thermal conditions
- for foundry operations



Results / Mass variation phenomena and kinetics: heating and cooling

- No clear dependence, on the Ni content, of the temperature of detectable mass gain due to oxidation: all oxidation start temperatures stay around 750°C
- No clear dependence, on the Ni content, of the total mass gain achieved during the whole heating
- Rather severe oxide scale spallation during the post-isothermal stage cooling; again, no clear dependence, on the Ni content, of the cooling time before mass loss start as well as of the final mass loss achieved at the test end



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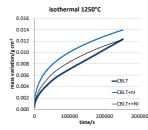
Results / Mass gain phenomena and kinetics: isothermal

stage

 All mass gain curves similar to parables: progressive thickening continuous external oxide scale covering surface; except the (Ni–free) CBLT alloy which was affected by linear mass gain after about 30 hours

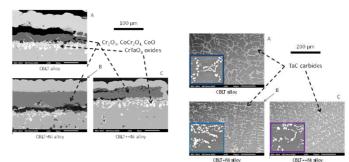
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- No clear dependence, on the Ni content, of the apparent mass gain achieved only during the isothermal stage; same remark about the "real" mass gains (corrected from chromia volatilization, using a 200 × 10⁻¹⁰ g cm⁻² s⁻¹ value for the Kv constant)
- All Kp constants (corrected from chromia volatilization) at the 600-700 \times 10⁻¹² g² cm⁻² s⁻¹ level



Results / Post-mortem observation: surface states, bulk microstructures after the induced {1250°C, 70h}-aging

- + External oxide scale with thickness in the [30 $\mu\text{m},$ 50 $\mu\text{m}]$ range
- Scale mainly made of chromia; but small presence of cobalt oxide and of spinel
- Internal oxidation: subsurface clusters of complex oxide involving chromium and tantalum
- Initial TaC population still present with similar quantities, but visible progress of fragmentation, coalescence and coarsening



Summary / Conclusions

- The progressive addition of nickel to the reference Ni–free cobalt–based alloy did not affect significantly the as–cast microstructures of the obtained alloys and their refractoriness.
- The evolution of the TaC carbides population was globally the same for the three alloys, with
 probably the same influence on the mechanical properties at elevated temperature
- No clear or no systematic influence of the nickel content was noticed concerning the oxidation behavior at 1250°C, except the sustainability of the "parabolic" regime of the isothermal mass gain kinetic.
- Since this is generally the difference in chromium diffusion easiness which is pointed out for the difference of oxidation resistance between cobalt alloys and nickel alloys, these differences are maybe not so marked at the particularly elevated temperature applied in this work (1250°C)
- Creep tests for comparison remain to be performed but, in the microstructure and oxidation resistance points of view, it appears beneficial, in this family of alloys, to replace, by nickel, a part of cobalt which is a critical element.

