

Search for the maximal threshold Co content for the oxidation behaviour point of view for 25wt.% Cr-containing TaC-strengthened cast superalloys designed for use at 1200°C on long time

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AERONAUTICS, POWER GENERATION, INDUSTRIAL TOOLS FOR SHAPING MOLTEN GLASSES ...

NEED OF HIGH TEMPERATURE MATERIALS

*Resistance against creep deformation,
oxidation and corrosion at high temperature*

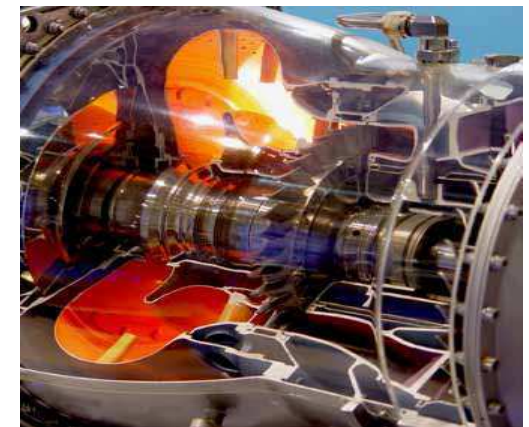
REFRACTORY METALLIC ALLOYS

e.g. Nickel or Cobalt-based Superalloys



ELABORATION WAYS:

*Powder Metallurgy, Mechanical Alloying,
Additive Manufacturing,
Oriented or Single crystalline solidification,
or simply classical polycrystalline foundry!*



EQUIAXED POLYCRYSTALLINE ALLOYS:

Rather old metallurgical principle but intrinsic advantages
(when carbides-strengthened alloys):

High toughness and resistance of the quasi-continuous dendritic network

High resistance of the discontinuous interdendritic skeleton of carbides

EUTECTIC MC-TYPE TANTALUM CARBIDES POTENTIALLY VERY INTERESTING:

Tendency of TaC to develop preferentially to chromium carbides in Cr-rich Co-based alloys

Script-like morphology and imbrication with matrix favoring interdendritic cohesion

Good stability of the MC carbides at elevated temperatures in Co-based alloys

IN THIS WORK:

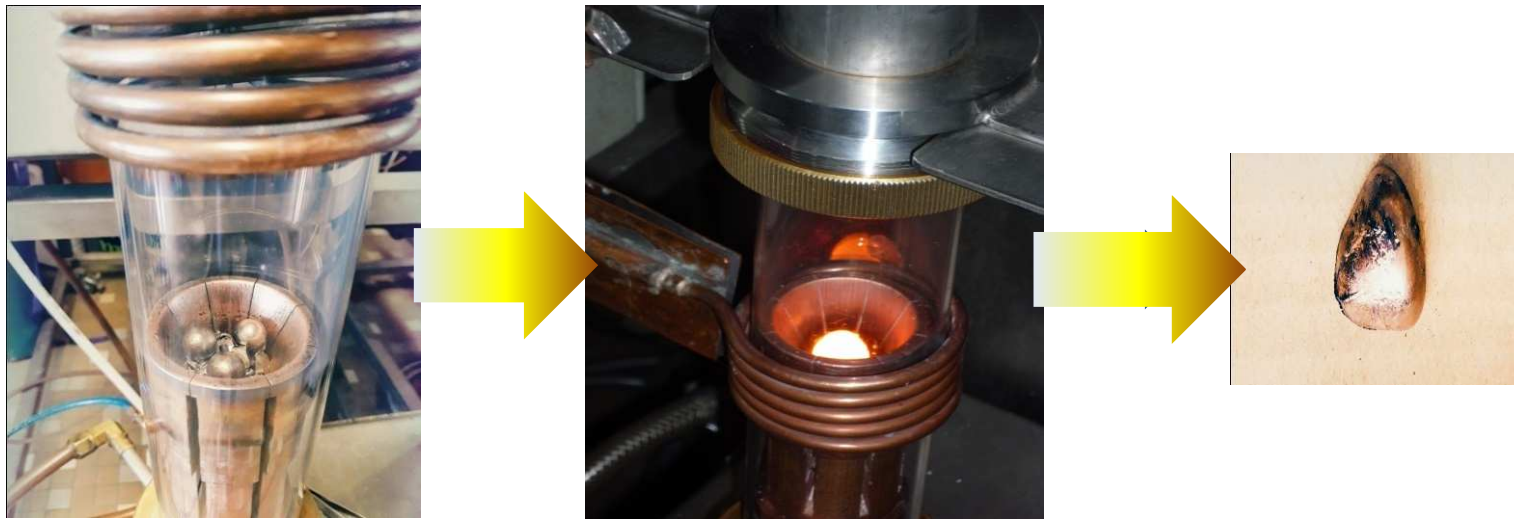
EXPLORING THE HEAT RESISTANCE OF ALLOYS DESIGNED TO BE STRENGTHENED BY TaC
AND TO RESIST OXIDATION & CORROSION USING PROTECTION BY CHROMIA
WITH A SPECIAL FOCUS ON THE Co/Ni RATIO FOR THE BASE ELEMENT ROLE

EXPERIMENTAL:

Exploring the microstructure evolution of Ni-rich alloys
when Co is progressively added instead Ni

with a series of {25%Cr – 0.4%C – 6%Ta}-containing (Ni,Co)-based alloys,
by increasing the Co/(Ni+Co) ratio from 0/5 (0C5N Ta) to 5/5 (5C0N Ta)

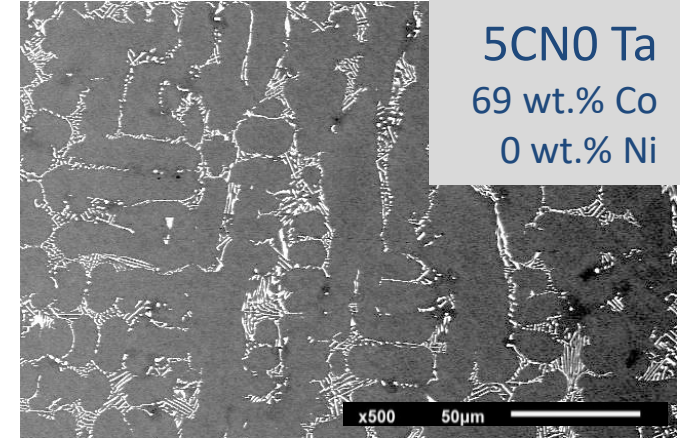
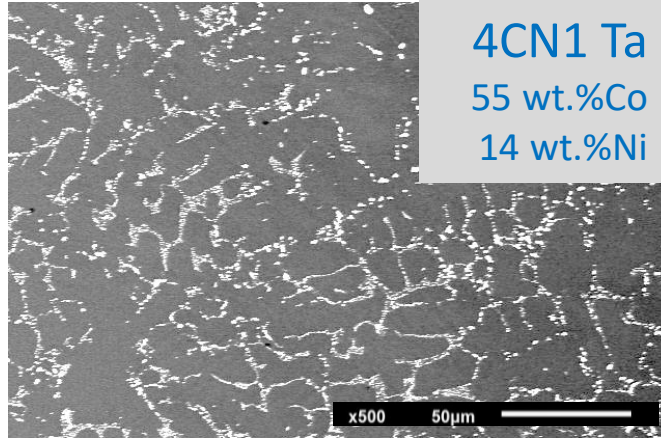
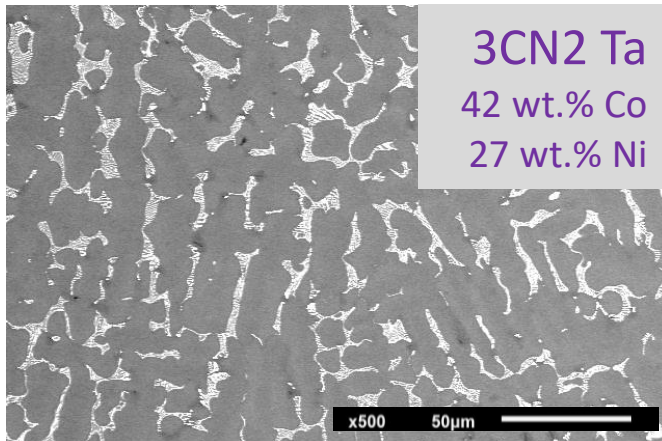
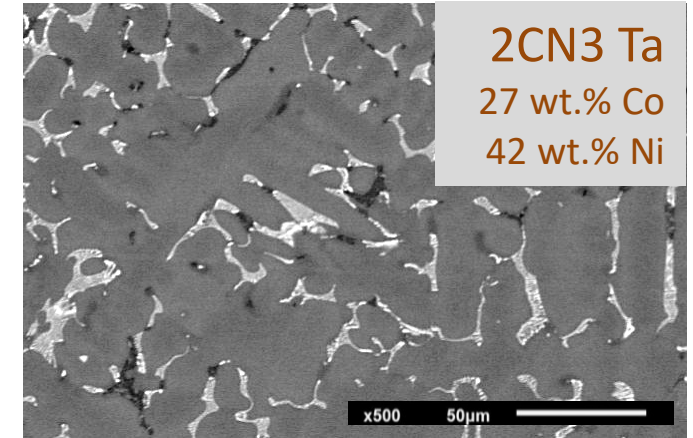
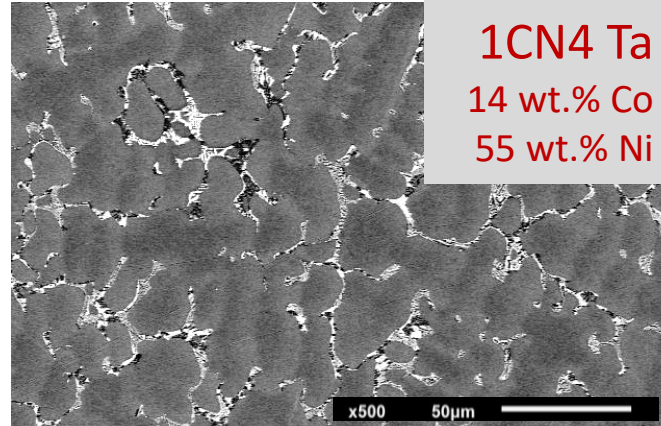
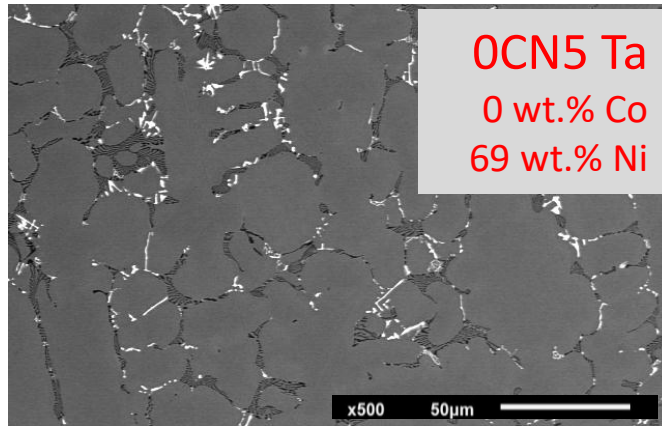
Elaboration of the alloys by High Frequency induction melting under Argon



*Examination of the microstructures of the obtained as-cast alloys
and after long exposure at high temperature (170 hours at 1200°C)*

→ To specify the oxidation by air and microstructure evolution for long time at 1200°C
with as objectives some recommendations for the Co content

AS-CAST MICROSTRUCTURES OF THE OBTAINED ALLOYS



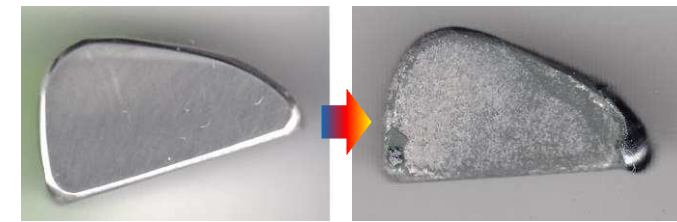
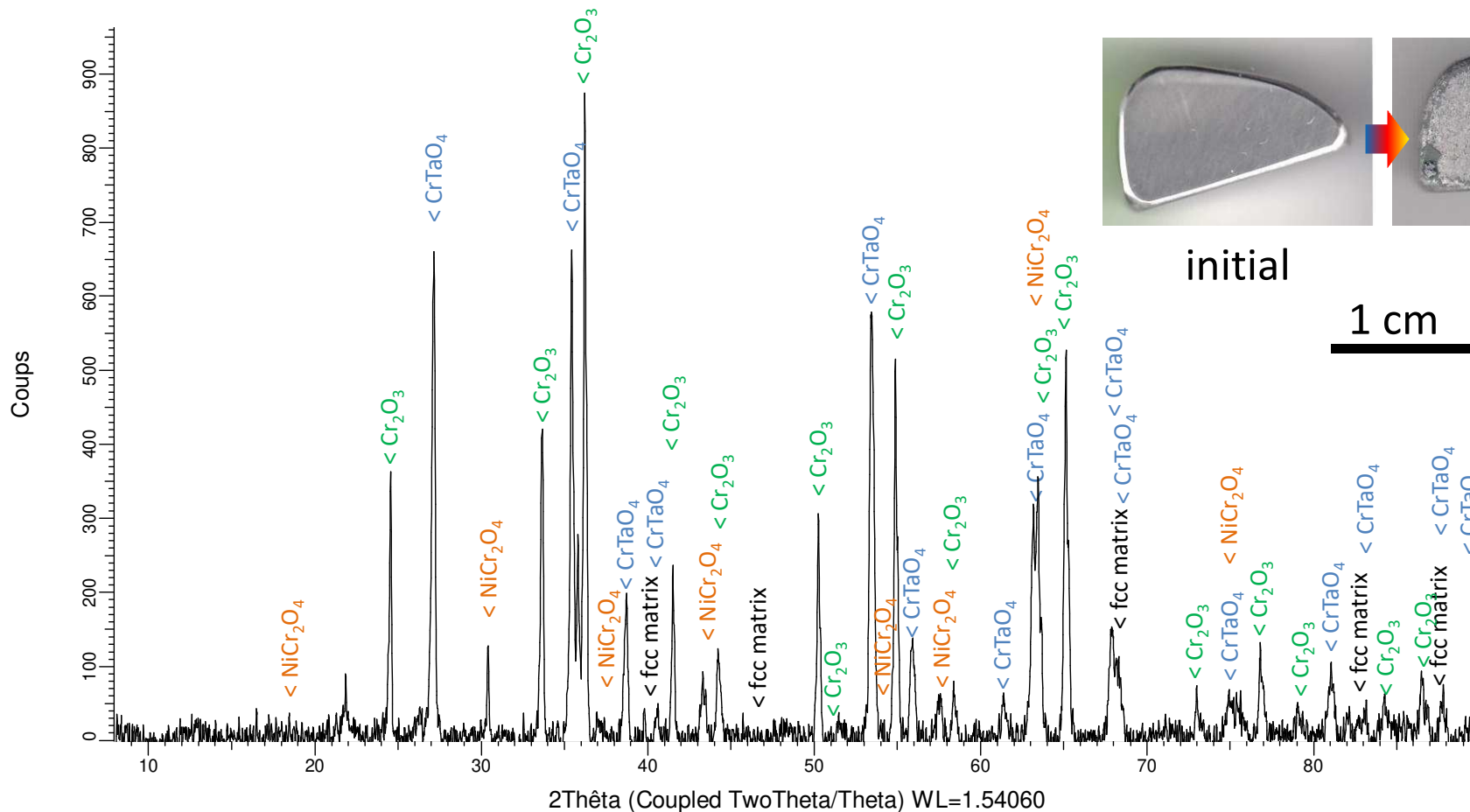
As-cast microstructures of the $x\text{Co} - (69-x)\text{Ni} - 25\text{Cr} - 0.4\text{C} - 6\text{Ta}$ alloys (wt.%)

- Polycrystalline dendritic microstructures
(grey {Co & Ni}-based austenitic solid solution of Cr, C and Ta)
- Double population of carbides in the three Ni-richest alloys: black Cr_7C_3 and white TaC
- Only TaC in the three Co-richest alloys

RESULTS: H. T. oxidation / surface states, XRD on spalled off oxides

After 170h in air at 1200°C:

- More or less severe oxidation depending on the Co part in the Ni + Co quantity
- More or less severe oxide spallation during cooling versus Co / Ni + Co again
- XRD on the oxides spalled off and collected in the shuttle: more or less extended denuded and different types of oxides



initial

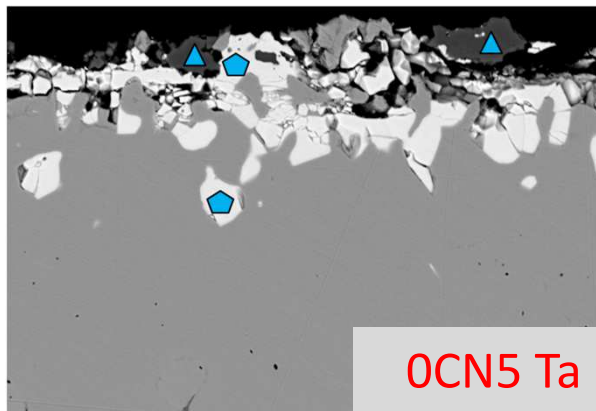
final

1 cm

XRD on the oxides lost by the 1C4N Ta alloy at cooling from 1200°C

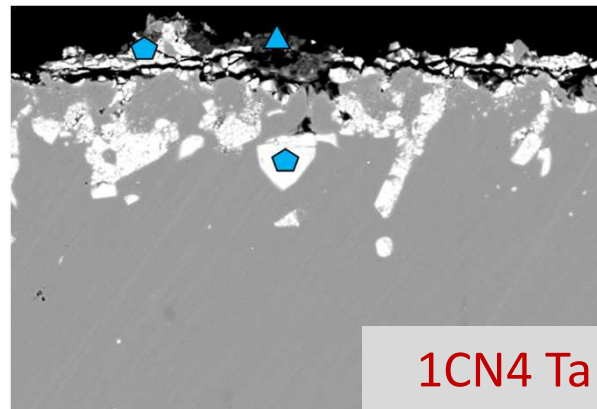
RESULTS: H. T. oxidation / cross-sectional oxides examination

Case of the three Ni-richest alloys



▲ : Cr_2O_3 ⬠ : CrTaO_4

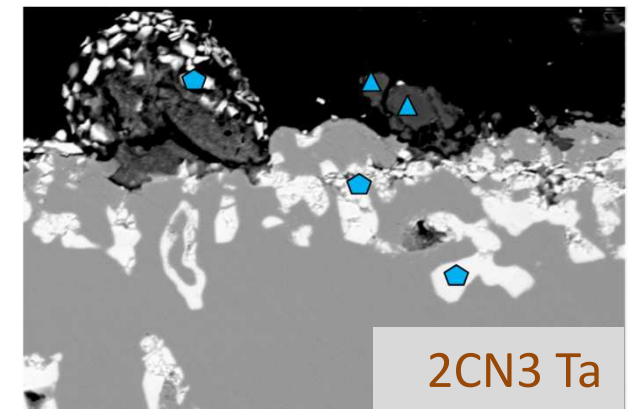
* Only rare parts of external oxide scale available for Identification / examination (but mainly chromia)



25 μm

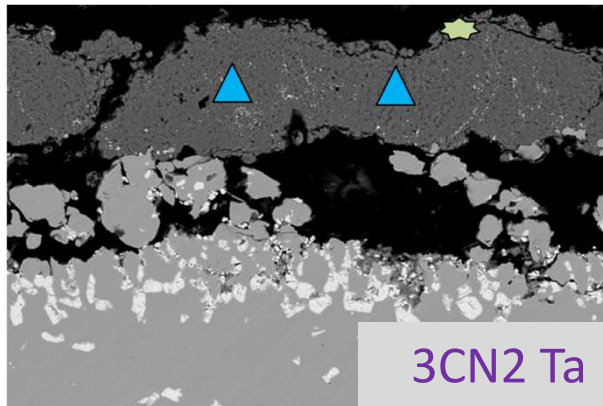
* Numerous islands of CrTaO_4 in subsurface close to the scale/alloy interface

* CrTaO_4 obviously also present in the scale, mixed with chromia



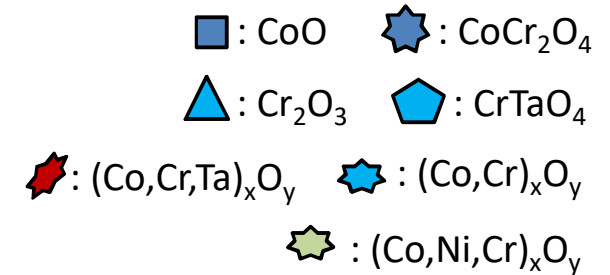
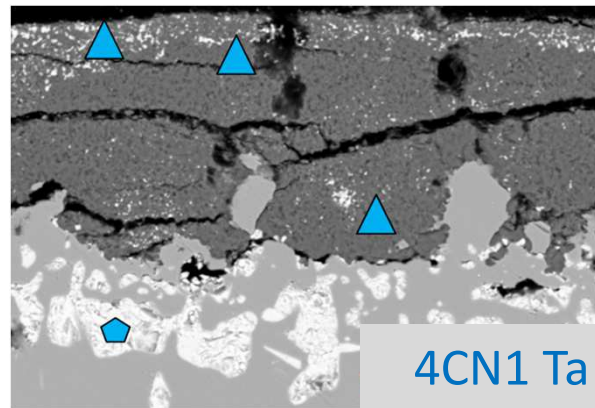
RESULTS: H. T. oxidation / cross-sectional oxides examination

Case of the three Co-richest alloys

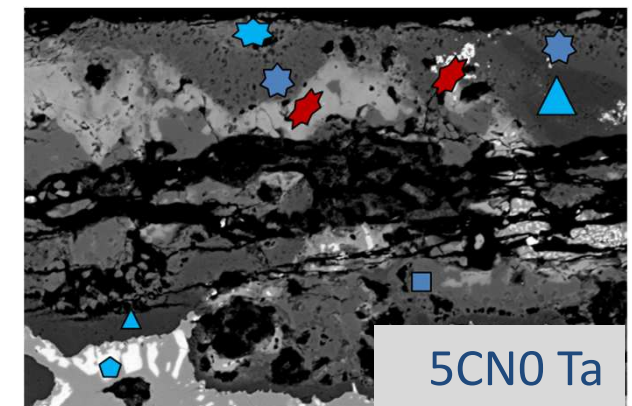


- Behavior worse than for the Ni-richest alloys
- Scales more present and thicker; inwards progress of oxidation

* Here and there: loss of the chromia-forming behavior; presence of cobalt oxides and of spinels



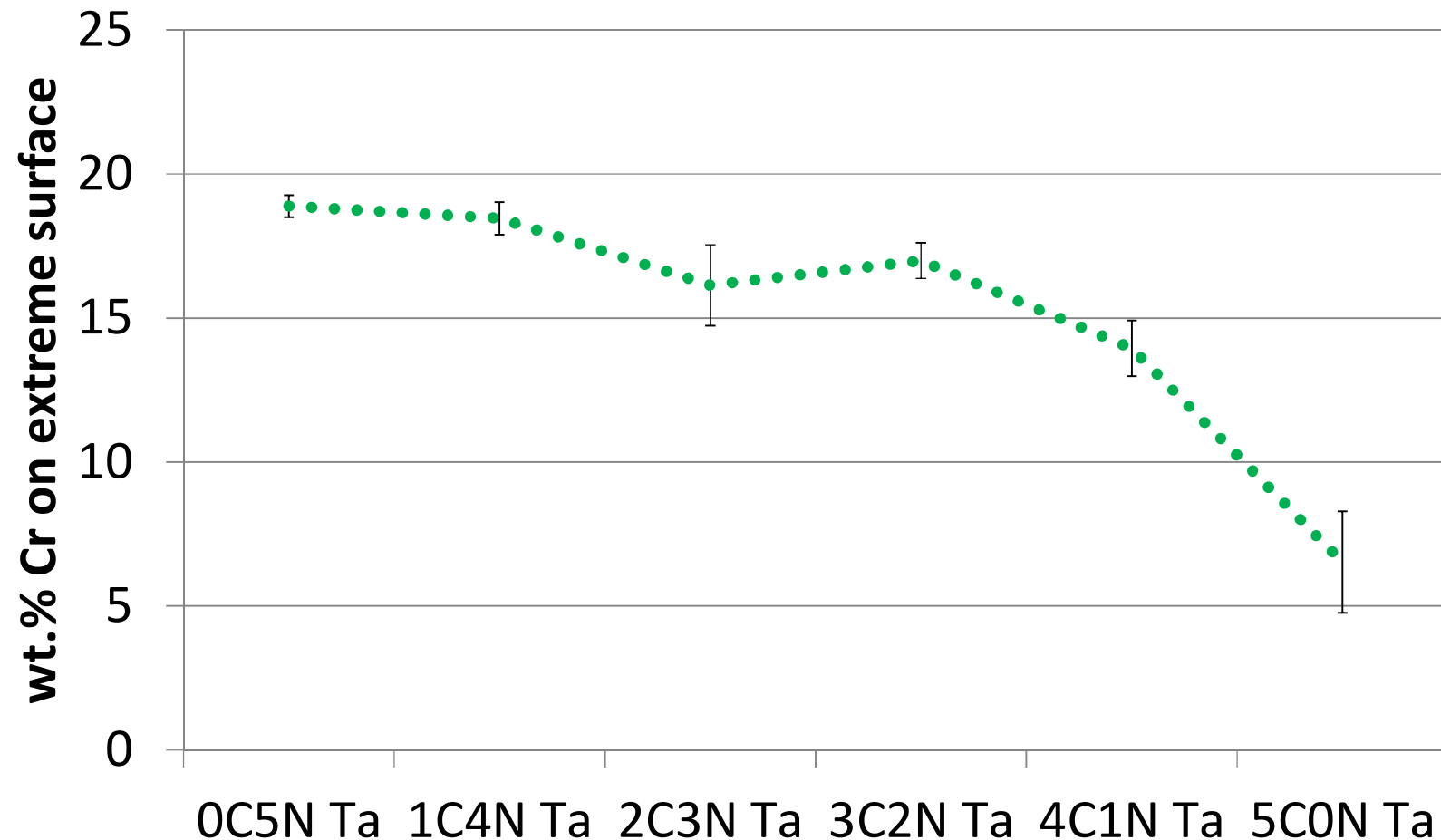
25 μm



RESULTS: H. T. oxidation / compilation of the observed oxides

Alloy	X-Ray diffraction	SEM/EDS
0CN5 Ta	NiO, NiCr ₂ O ₄	/
1CN4 Ta	NiCr ₂ O ₄	/
2CN3 Ta	CoCr ₂ O ₄	/
3CN2 Ta	CoCr ₂ O ₄	(Co,Ni,Cr) _x O _y , CoCr ₂ O ₄
4CN1 Ta	CoCr ₂ O ₄	(Co,Ni)O, CoCr ₂ O ₄ , (Co,Ni,Cr) _x O _y
5CN0 Ta	CoCr ₂ O ₄	CoO, CoCr ₂ O ₄ , (Co,Cr) _x O _y , (Co,Cr,Ta) _x O _y
+ in all cases:	Cr ₂ O ₃ and CrTaO ₄	Cr ₂ O ₃ and CrTaO ₄

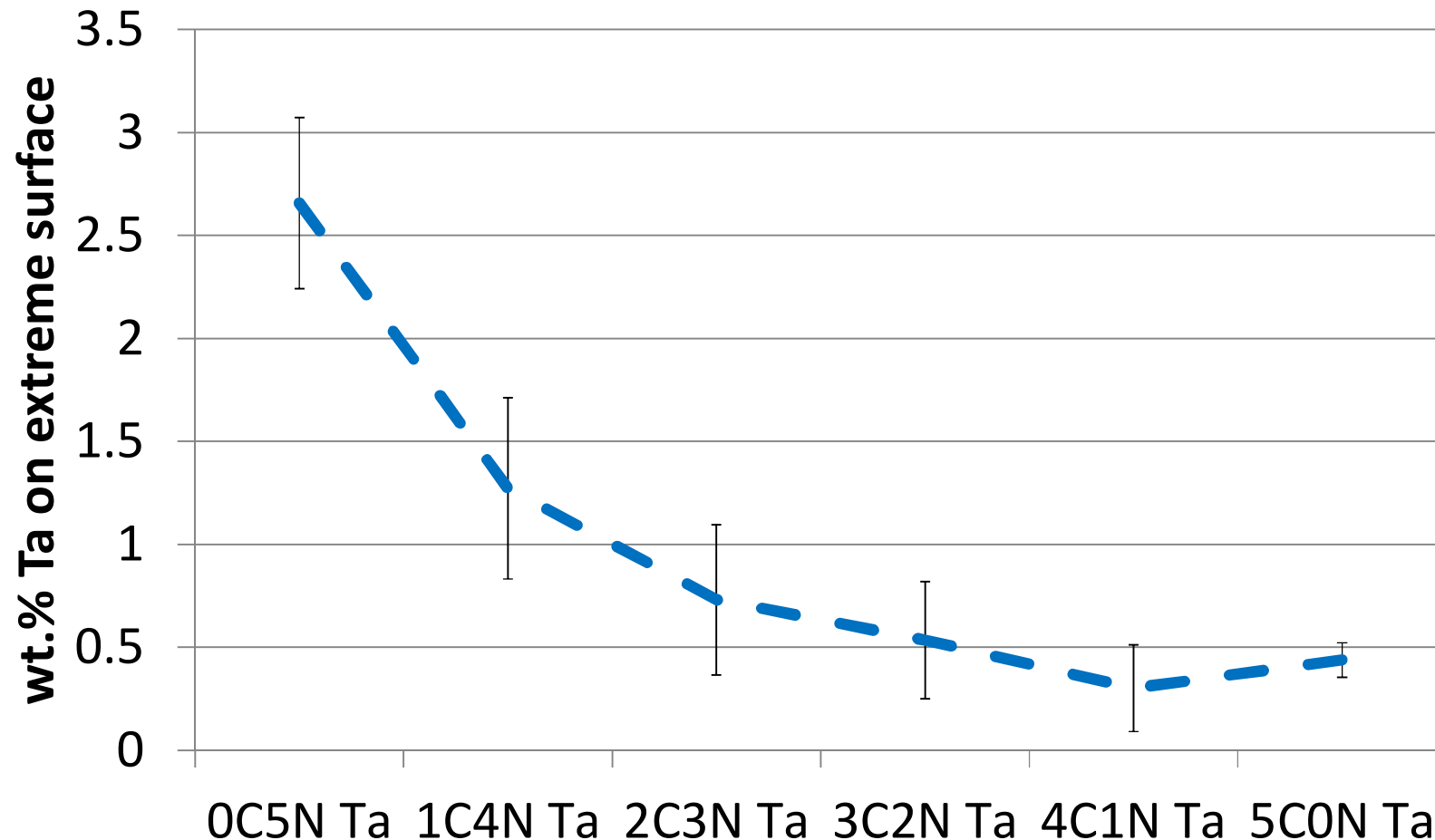
RESULTS: oxidation behavior / Cr and Ta depletion in subsurface



Chromium:

- The four Ni-richest alloys: Cr content decreased close to the oxidation front, but still high enough for the sustainability of the chromia-forming behavior
- The two Co-richest alloys: Cr content low, and even very low in some locations; imminent loss of the chromia-forming behavior or general catastrophic oxidation already started

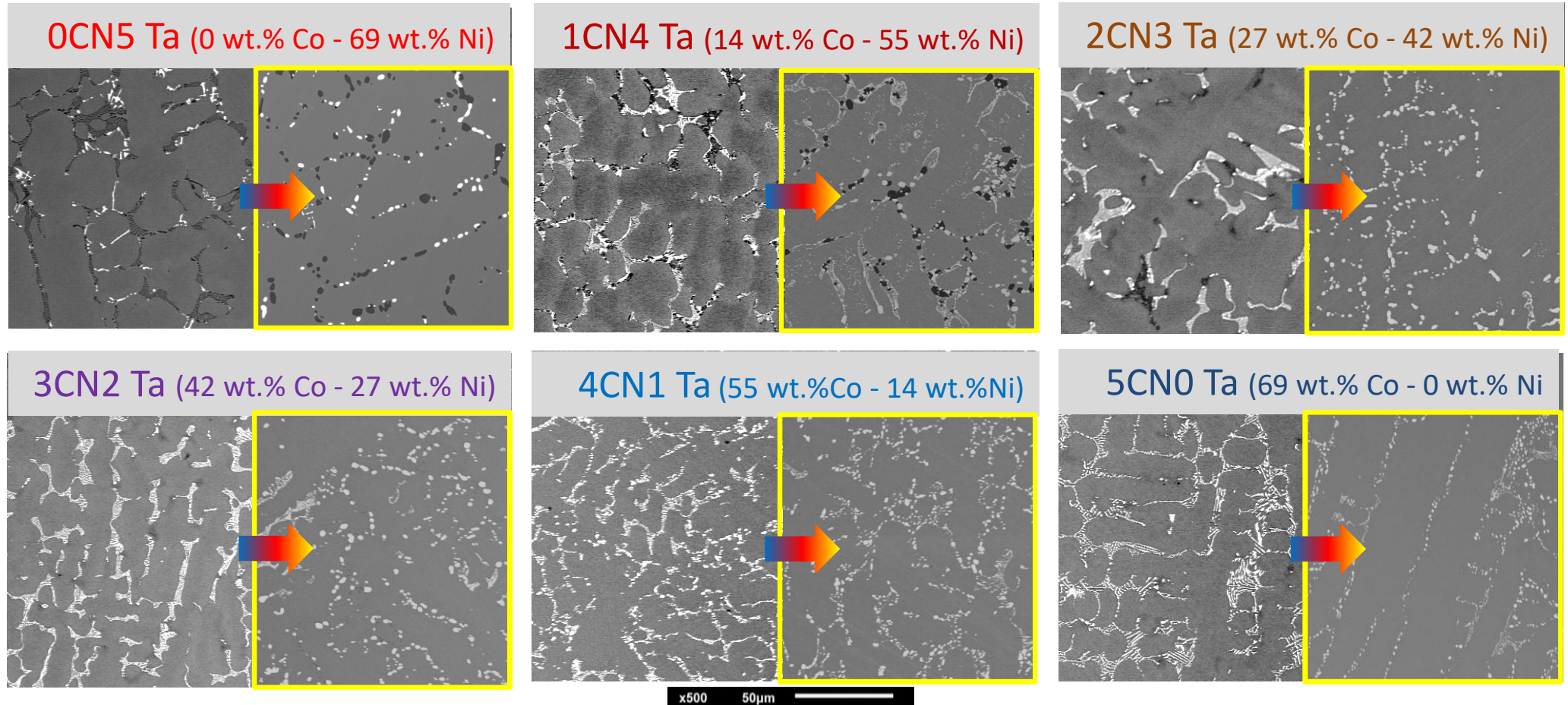
RESULTS: oxidation behavior / Cr and Ta depletion in subsurface



Tantalum:

- Regular decrease in weight content when the Co part increases at the expense of Ni
- Due to oxidation but also to the initial carbide population (more TaC in the microstructure for alloys with high Co than for alloys with high Ni)

RESULTS: heat-induced modifications of the bulk microstructures



Aged microstructures of the $x\text{Co} - (69-x)\text{Ni} - 25\text{Cr} - 0.4\text{C} - 6\text{Ta}$ alloys (wt.%)

- Decrease in volume fraction and coarsening for the Cr_7C_3
- Decrease in volume fraction and fragmentation for the TaC
- Cr, Ta and C enrichment of the matrix

SUMMARY / CONCLUSIONS

- * 170 hours spent at 1200°C: very severe work conditions for such alloys (notably the particularly high temperature!)*
- * Taking that into account: rather good isothermal oxidation behavior of the three nickel-richest alloys and therefore ...*
- * ... the Co content must be chosen lower than the Ni one for the HT oxidation point of view (this was confirmed in a parallel work by thermogravimetric measurements at other temperatures)*
- * Unfortunately: too easy loss of the protecting chromia scale when temperature decreases, even slowly; especially true for the nickel-richest alloys*
- * The lack in resistance against scale spallation: probably due to the subsurface CrTaO_4 ; this point remains to be significantly improved, e.g. by introduction of R.E.*
- * For the HT mechanical resistance point of view: the carbide network of TaC is favoured by Co addition; Co is both favorable for TaC-strengthening and detrimental for HT oxidation !!*
- * Regardless to the carbides' types, the carbide network became deteriorated in all alloys (investigations are in progress for characterizing the real consequences on creep)*

*Thank you for
your attention*

