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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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Abstract. The base of chromia-forming cast superalloys is the most often constituted of nickel and/or cobalt. Both elements may be simultaneously present, for instance Co for promoting good mechanical properties and Ni for stabilizing the austenitic matrix and favouring good ductility and machinability. In service, superalloys must also resist hot oxidation, property favoured by Ni but disadvantaged by Co. In (Ta,C)-rich cast superalloys exposed at high temperature, the intergranular strength may be enhanced by the very efficient TaC carbides while the higher the Co content the stronger the matrix creep resistance. In this work, six alloys designed to be chromia-forming and TaC-strengthened were exposed to laboratory air at 1200 °C for 170 hours, to examine how the deterioration by oxidation and the evolution with time of the strengthening carbides in the bulk may be influenced by the Co/Ni ratio in the case of this important family of superalloys. The characterization of the formed oxide scales and of the morphologic evolution of the carbides allowed identifying a {0.6Co-0.4Ni}-proportion for the base elements. Such combination obviously allows keeping a chromia-forming behaviour and a good adherence of the protective oxide scale on the alloy, as well as a good resistance of the TaC against fragmentation.

1. Introduction

The superalloys based on nickel and/or cobalt represent the major family of metallic refractory alloys used on long times at high temperature in severe chemical and mechanical conditions [1]. Despite the more or less recent new ways of elaboration (additive manufacturing, single-crystalline solidification), fabrication by conventional casting still exists and keeps on offering high performance superalloys for geometrically complex components [2]. The high degree of interconnection of their matrixes and the equiaxed obtained structures allow high and isotropic creep strength, properties that remain interesting for many applications for which the high performance microstructures of γ/γ' single crystals cannot be successfully achieved [3]. Many turbine disks (and even some blades) for aeronautics or power generation as well as the most of the high speed rotating glass forming tools are still made of superalloys of this kind.

Being solid solution strengthened or reinforced by the intra-dendritic fine and dense precipitation of hard particles (carbides, intermetallic compounds) is compulsory for achieving high creep resistance of the matrix. For instance heavy atoms such as tungsten may improve this property in cast nickel-



based superalloys [4]. But tantalum, and also cobalt despite its lower atomic mass, may play such role. To complete the resistance against high temperature creep, the interdendritic spaces and grain boundaries of the equiaxed cast superalloys must be strengthened by hard and stable coarse particles interlocking neighbor dendrites. This can be successfully achieved by TaC carbides, but more in Co-rich superalloys [5,6] than in Ni-rich superalloys [7]. Co-rich nickel-based or cobalt-based superalloys obtained by conventional casting take benefit from matrix strength due to cobalt and efficient TaC-strengthening enhanced by the high presence of Co. On the other hand it is well known that the oxidation behaviour at high temperature of these alloys, necessarily based on chromium rather than on aluminium, is far from excellent but it can be improved by addition of Ni [8,9].

So, the main question for conventionally cast superalloys based on cobalt and/or nickel and the high temperature strength of which is based on solid solution hardening by Co and Ta dissolved atoms and on the interlocking by TaC carbides, is: what can be the Co/Ni ratio leading to the best compromise of high temperature mechanical and chemical behaviours? The purpose of the present study is to try responding this question for alloys containing 25wt.%Cr for favouring a chromia-forming oxidation behaviour and 0.4 wt.%C and 6 wt.%Ta for favouring the presence of TaC interdendritic carbides in optimized proportion.

2. Materials and methods

Six alloys were previously elaborated by high frequency induction melting for a thermodynamic study [10], with the form of 40g-weighing ingots. These alloys were designed to contain 25wt.%Cr, 0.4wt.%C and 6wt.%Ta. The remaining 98.6wt.% were composed of:

- only nickel for the “0CN5 Ta” alloy and only cobalt for the “5CN0 Ta” alloy
- n fifths of Co and (5-n) fifths of Ni for the “nCN(5-n) Ta” alloys named from “4CN1 Ta” to “1CN4 Ta”

The global chemical compositions and the as-cast microstructures of these alloys were controlled again, on parts taken in the same location in ingot as the samples for the oxidation tests of this study. This was carried out using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS).

Six other parts, each of about 10g with a planar face ground with #1200-grit SiC papers, were placed in a muffle furnace, each in a fairly large alumina shuttle. The applied heating was of 20 °C/min up to 1200 °C. The duration of the isothermal stage at 1200 °C was 170 hours. It was finished by a cooling in the closed furnace after shut-off.

After return at room temperature, each oxidized sample was carefully handled and embedded in a metallographic cold resin mixture. For each oxidized sample, the parts of the external oxide scale which spalled off during the cooling were collected and subjected to X-ray diffraction (XRD) with a Philips X'Pert Pro diffractometer (Cu K α , $\lambda = 1.541 \text{ \AA}$) for their identification.

The embedded samples were cut into two parts. Each half was ground and polished until a mirror-like state. The obtained metallographic samples were examined by SEM in Back Scattered Electrons (BSE) mode using a JEOL JSM-6010LA electron microscope. Spot EDS analyses were carried out to identify the oxide natures in the parts of the external scale still attached to the alloy as well as the internal oxides. Spot analyses were also performed to value the chemical composition in the alloy close to the alloy/external scale interface, with special attention to the local contents in Cr and Ta.

3. Results & discussion

3.1. Microstructures

The chemical compositions of the alloys were found to be very close to the wished contents in Co, Cr, Ta and Ni. This verification of the C content was not possible, because of the too low molar mass of this element and of its targeted low content (0.4wt.%); however, by considering first that the applied elaboration protocol usually leads to a very good respect of the obtained C content by comparison to the wished one, and second that the obtained quantity of carbides is typical of this C content, it was assumed that all the six alloys really contain very close to 0.4wt.%. Concerning the initial microstructures of the alloys (figure 1), they are themselves totally similar to the ones of the alloys

previously studied [10, 11]. To resume them, one can say that all the alloys are composed of a dendritic matrix and of carbides of one or two types, forming a eutectic compound with matrix in the interdendritic spaces. The three nickel-richest alloys (upper micrographs: “0CN5 Ta”, “1CN4 Ta” and “2CN3 Ta”) contain acicular-shaped eutectic chromium carbides (of the M_7C_3 type) and Chinese script eutectic tantalum carbides (TaC) while the three cobalt-richest alloys approximately contain only script TaC carbides.

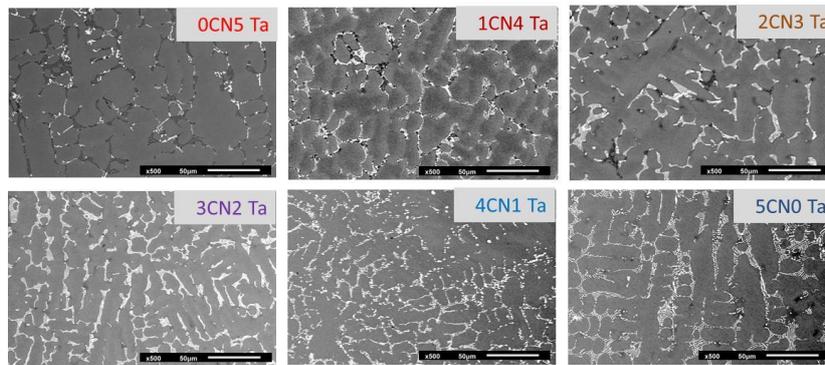


Figure 1. The initial microstructures of the alloys

Before examining the high temperature corrosion products one may have a look to the new bulk microstructures of the {1200 °C, 170h}-exposed samples (figure 2). In the core of these samples, the microstructures were possibly changed, because of the high temperature stay but not altered by the surface oxidation reactions. The carbides morphologies were more or less modified. The chromium carbides significantly changed for becoming coarse globular carbides (“0CN5 Ta” and “1CN4 Ta” alloys) while they totally disappeared in the “2CN3 Ta” alloy which contain only TaC carbides with here and there curious shapes. The script-like TaC carbides initially present in the two Ni-richest alloys themselves turned into globules (fragmentation followed by coarsening). In contrast, the script-like tantalum carbides well resisted this morphologic evolution tendency, particularly the “5CN0 Ta” alloy. Knowing the deleterious effect of the fragmentation of the carbides and of their coarsening as globules on the mechanical properties at high temperature, these observations suggest that the Ni-richest alloys may have lost the main part of their resistance against creep, in contrast with the Co-richest alloys the creep-resistance of which can be expected to stay at a high level.

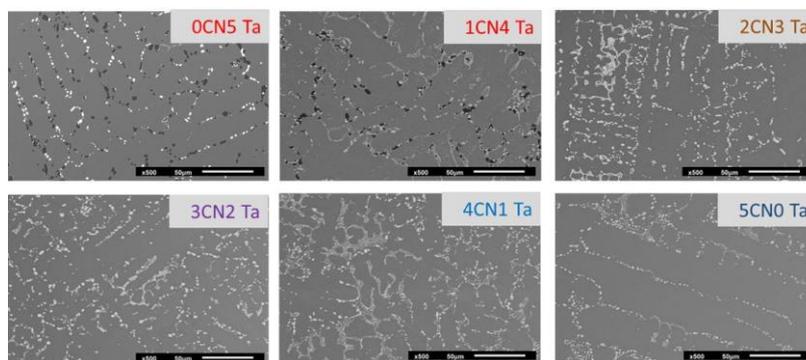


Figure 2. The bulk microstructures after the {1200 °C, 170h}-stay

3.2. Oxides formed externally and internally

Concerning the high temperature corrosion products, the first important observation which can be made concern the more or less intense loss of the external oxide scale during the cooling. Obviously,

the three Ni-richer alloys were particularly affected by this phenomenon since only some rare parts of the oxide scale still existing near the end of the isothermal stage can be observed on the metallographic samples. In contrast, the oxide scale seems having been more adherent to the surface of the Co-richer alloys. Thus, to totally specify the oxides formed during the 170 hours spent at 1200 °C it was really necessary to analyse both the oxides remaining in the shuttle and the oxides still attached to the samples. The X-ray diffractograms performed on the mix of oxide parts collected in the ceramic shuttle after test allowed identifying the formed oxides belonging to the spalled-off parts of the oxide scales (figure 3: example of the “1CN4 Ta” alloy). This was completed by the cross-sectional characterization (BSE imaging and EDS analyses) on the embedded and polished samples (figure 4). The results of XRD and SEM/BSE identification of the oxides formed over the samples and in the sub-surfaces are summarized in table 1.

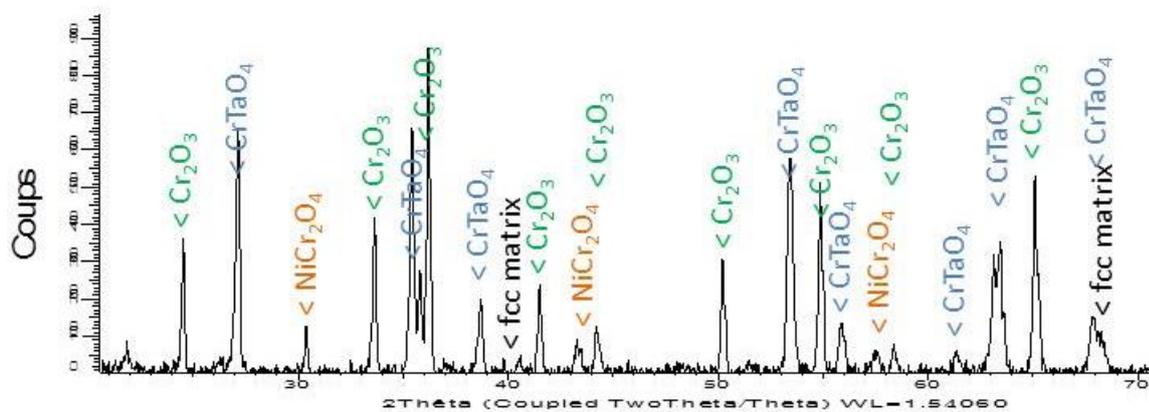


Figure 3. Diffractogram of the oxides detached from the 1CN4 Ta alloy

The diffractograms resulting of the XRD analyses of the six oxide powders collected in the six shuttles all show that chromia (Cr_2O_3) and the oxide of Cr and Ta (CrTaO_4) are present in all cases. The spinel oxides (NiCr_2O_4 for “0CN5 Ta” only, CoCr_2O_4 for the five other alloys) also formed systematically. One can also note the presence of NiO which formed probably as an outer part of the external scale, as this is usual for Ni-based alloys. The oxides still present on the samples after return to ambient temperature are more complex. They mainly concern the three Co-richer alloys. The best illustration is given by the cobalt-based “5CN0 Ta” alloy (micrograph in figure 4 and oxide description in table 1). In addition it is obvious that the higher the Co content in these Co-richer alloys, the higher the scale thickness and the more complex the composition of the scale.

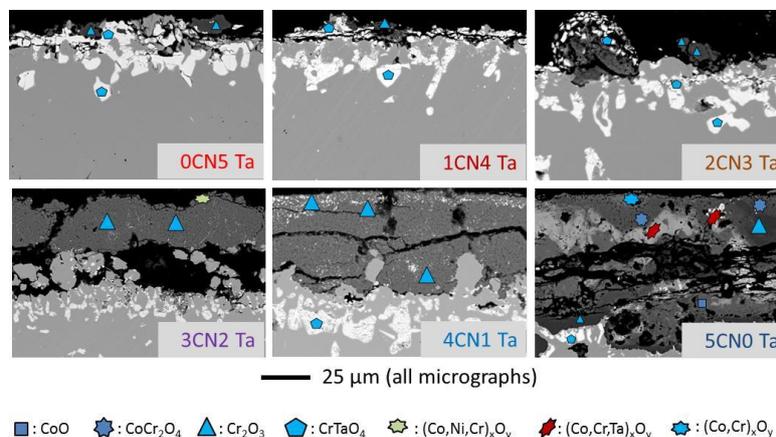


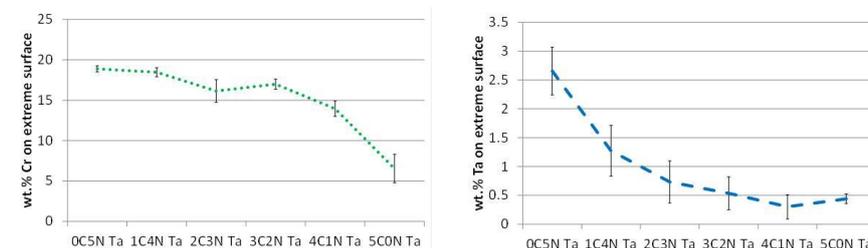
Figure 4. Characterization of the oxidized states of the alloys’ surfaces

Table 1. Synthesis of the oxides' identifications

	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

The chemical composition of the outermost parts of the alloys (close to the alloy/oxide scale interface) was measured by EDS spot analysis. The results concerning Cr and Ta are both plotted in figure 5. It obviously appears that the higher the Co content in the alloy the lower the Cr content in extreme surface. The decrease in Cr is furthermore more marked when the alloy becomes Co-based instead Ni-based (the Cr content becomes lower than 15wt.% for the “4CN1 Ta” alloy). For tantalum, the Ta decrease is the fastest when Co starts to replace Ni in the Ni-richest alloy.

These results show that these are now the Co-richest alloys which present the worst behaviours. Their oxide scales are composed of multiple oxides, much less protective than the chromia layer which efficiently prevented fast oxidation of the Ni-richest alloys, as suggested by the Cr and Ta contents in extreme surface remained rather high. The loss of the chromia-forming behaviour of the Co-richest alloys, resulting in a general oxidation of all the base elements into single or mixed oxides, is in good agreement with the Cr contents on extreme surface become particularly low.

**Figure 5.** The Cr (left) and Ta (right) contents in extreme surface

4. Conclusion

Globally, one can consider that the TaC-reinforced {Co, Ni}-based alloys behaved rather well during the applied oxidation test, by considering the particularly high level of temperature and long exposure. The currently best superalloys, the γ/γ' Ni-based single-crystals, are much better in term of oxidation resistance but lose their excellent creep resistance as soon as the service temperature becomes higher than 1100 °C. Some of the present alloys – the Co-richest ones – are obviously able to keep almost intact their script-like TaC carbides at 1200 °C, even until 170 hours of isothermal exposure. The problem is that their oxidation resistance is not good enough. Fortunately, adding Ni in sufficient quantity (2/3 of Co replaced by Ni: “3CN2 Ta” alloy) may lead to a not perfect but much better oxidation resistance without significantly deteriorating the population of the strengthening TaC carbides. The investigation of the performances of this alloy merits to be deepened, notably by real creep tests at this temperature of 1200 °C.

To finish, one can remark that the influence of the Ni/Co ratio, notably the beneficial effect of Ni on the high temperature oxidation resistance observed here, is in good agreement with observations made in previous works. What needs to be underlined here is that the present results especially concern new alloys which are especially rich in Ta (6wt.%, much higher than many superalloys) and designed to

contain exclusively TaC carbides by the choice of the same molar contents for Ta and C (chemical design which appears here to be successful only for Ni contents not too high).

Acknowledgments

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