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Behavior of Cast {Ti or Ta}-Containing Alloys Based on Nickel and/or Cobalt in High Temperature Oxidation: Effect of the Ni/Co Ratio

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Abstract: Many of the cast superalloys chosen for specific applications at high temperatures, such as tools devoted for shaping molten glass, are based on nickel or cobalt. They contain chromium and carbon to achieve good resistances against both mechanical stresses and hot oxidation/corrosion, by favoring the formation of reinforcing carbides at solidification and the development of a protective oxide scale of chromia during service. In presence of tantalum or titanium in the chemical composition of the alloys, high performance MC carbides may be obtained but this depends on the base element. One recently observed how the respective proportions of nickel, cobalt and chromium may promote the formation of TiC or TaC at the expense of chromium carbides. The ratings chosen for Ni, Co and Cr may have high influence on the oxidation of the alloys at high temperature this is what was studied in this work.

Keywords: Superalloys; Titanium; Tantalum; Carbides; High Temperature Oxidation

1. Introduction

Among the earliest refractory metallic alloys available for applications at high temperature in conditions of mechanical stresses and chemical aggressiveness of fluids, the polycrystalline superalloys based on cobalt and/or nickel, elaborated by casting and containing chromium in their chemical compositions for resistance against hot oxidation and corrosion^[1] and carbides for resisting mechanical deformation such as creep^[2], may be still used in some cases today. By comparison with their early first versions these alloys can be more efficiently strengthened by optimized solid solution hardening and by new carbides more stable at high temperature on long times in term of volume fraction and morphology. MC carbides are currently under great interest since their script-like morphology inherited from their growth process during the eutectic part of the solidification of the alloys is particularly efficient for strengthening both grain boundaries and interdendritic spaces. Titanium monocarbides^[3] (TiC) and tantalum monocarbides^[4] (TaC) are very stable at elevated temperatures in chromium-rich cobalt-based alloys but it is not the case in the Ni-based versions. Indeed, in presence of 25 to 30 wt.%Cr, compulsory to allow oxidation and corrosion high enough at high temperature, Cr competes with Ti or Ta in the formation of carbides. In the best case two types of carbides (e.g. Cr₇C₃ and TaC^[5]) co-exist in similar proportions and in the worst case chromium carbides may be the single carbide phase present (e.g. Cr₇C₃ and TiC^[6]). Recently, two potential solutions to favor the appearance of MC only in case of molar or atomic parity between M and C were explored: adding more and more cobalt instead nickel (for TaC^[7] or for TiC^[8]), and varying (notably decreasing) the chromium content (e.g., for TaC^[9]). Unfortunately this was not really successful in most of cases, even if a slight tendency of improvement was sometimes observed.

Beyond the initial MC stability problematic it appeared possible to take benefit from the availability of these alloys (all of the type {Ni and/or Co, base} & 25Cr or xCr & 0.4C & 6Ta, in wt.%) to undertake a study of the influence of the

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Ni/Co ratio and of the Cr content on the behavior of these alloys at high temperature. Presenting some of the obtained results is the aim of the present work.

2. Experimental

2.1 Origin of the alloys support of this study

Initially several series of alloys were synthesized as compact ingots of about 40 grams. This was done by mixing the pure elements weighed at the required masses and by using a High Frequency induction furnace to melt the mixed under an inert atmosphere. After solidification and total cooling they were cut in several parts for carrying out the microstructures investigations.

2.2 High temperature oxidation runs

Parts remaining from the previous studies were prepared (ground with #1200-grit SiC papers) to be exposed isothermally at high temperature in an oxidant atmosphere. This was done in a muffle resistive furnace. Several types of oxidation tests were performed:

- 20 hours at 1127°C for the (Ni, xCo)-25Cr-0.4C-1.6Ti alloys
- 24 hours at 1127°C or 1237°C for the (Ni, xCo)-25Cr-0.4C-6Ta alloys
- 24 hours at 1127°C or 1237°C for the (Ni, $0 \leq xCr \leq 50$)- 0.4C-6Ta alloys

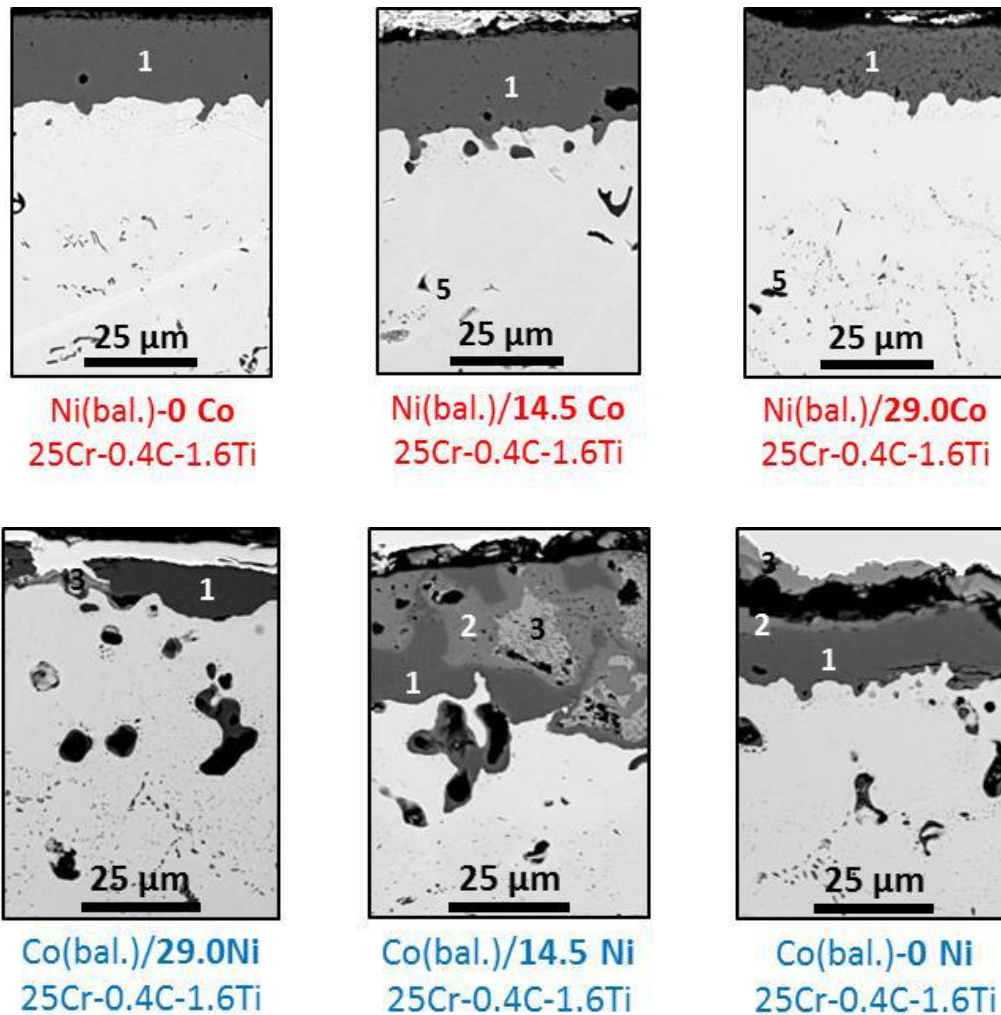
2.3 Metallography preparation and observation

After total cooling the oxidized samples were embedded in a cold resin mixture than cut, ground and polished until obtaining a mirror like state. They were examined in cross-section by Scanning Electron Microscopy (SEM) mainly in the Back Scattered Electrons (BSE) mode, and characterized by Energy Dispersive Spectrometry (EDS) to specify the oxides which formed externally or internally.

3. Results and discussion

3.1 The (Ni, xCo)-25Cr-0.4C-1.6Ti alloys oxidized at 1127°C

The six alloys based on Ni+Co and all containing 25wt.%Cr, 0.4wt.%C and 1.6wt.%Ti after exposure during 20 hours with as environment the laboratory air at 1127°C were oxidized following different mechanisms (Figure 1), depending on the Co/Ni balance. For the Co-free and the moderately Co-enriched alloys the oxidation behaviour was clearly chromia-forming. The external oxide is exclusively made of Cr₂O₃ and this scale is very compact, and furthermore very protective. When the Co content comes close to 30wt.% a first sign of degradation is the porous state of the chromia layer (which is however still the single oxide present). For higher Co contents (the considered alloys are henceforth Co-based and no longer Ni-based) the chromia-forming behavior begins to be lost. The oxide of Co and Ni, (Co,Ni)O, and the CoCr₂O₄ spinel oxide co-exist with Cr₂O₃. The behavior in oxidation of the alloy becomes logically similar to many cobalt-based alloys not very rich in Cr (here: 25 wt.%Cr lower than the 30wt.%Cr considered as compulsory for Co-based alloys to be able to behave as chromia-forming. Titanium, initially shared between the TiC carbides (black and script-like in the bulk) and the matrix (Ti in solid solution), takes part to oxidation at a lower scale, by internal oxidation close to the alloy/oxide scale interface, and also by the formation of a thin titanium oxide external scale located at the other side of chromia (this outer titanium oxide is often lost because of spallation or breakage during the handling of the oxidized samples).

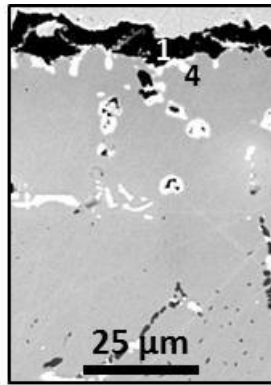


1: Cr₂O₃, 2: CoCr₂O₄, 3: (Co,Ni)O or CoO, 4: TiCr₂O₄, 5: TiO₂

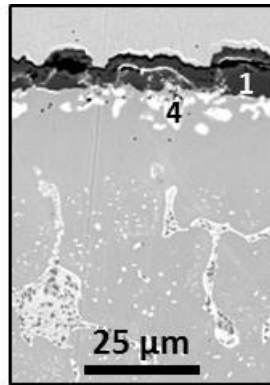
Figure 1; Cross-sectional observation of the oxidation results for the (Ni, xCo)-25Cr-0.4C-1.6Ti alloys oxidized at 1127°C for 20h.

3.2 The (Ni, xCo)-25Cr-0.4C-6Ta alloys oxidized at 1127°C and 1237°C

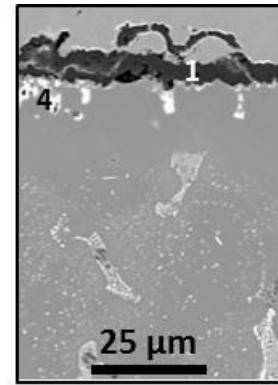
Figure 2 (1127°C) and **Figure 3** (1237°C) illustrate the oxidized states of the six alloys based on Ni+Co and containing 25wt.%Cr, 0.4wt.%C and 6wt.%Ta. Here too the Co-poorest alloys display a chromia-forming behaviour but the external scale is not of a so good quality as for the corresponding Ti-containing alloys oxidized at 1127°C. Chromia is the single main oxide present externally as long as the alloy contains more nickel than cobalt while oxides of nickel or of nickel + cobalt, (Co,Ni)O or CoO, and the spinel CoCr₂O₄ co-exist with chromia as soon as cobalt exceeds nickel in the alloy composition. The CrTaO₄ which classically forms in such alloys is always present in the sub-surface very close to the alloy/oxide interface, and films of this oxide can be seen also mixed with the external scale of chromia. The average thickness of chromia as well as the amount of CrTaO₄ (mainly in the subsurface) are logically higher when the exposure temperature was higher. More visible than in the case of the TiC-containing alloys previously commented, the carbide-free zone which developed from the alloy/external oxide interface is deeper for 1237°C than for 1127°C for all alloys.



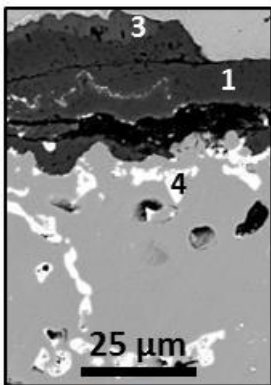
Ni(bal.)-0 Co
25Cr-0.4C-6Ta



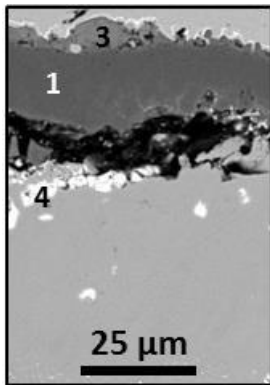
Ni(bal.)/14.5 Co
25Cr-0.4C-6Ta



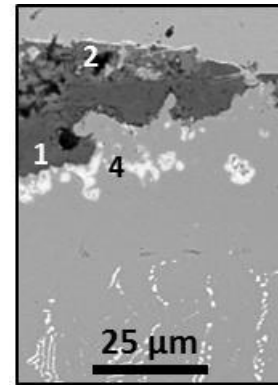
Ni(bal.)/29.0 Co
25Cr-0.4C-6Ta



Co(bal.)/29.0Ni
25Cr-0.4C-6Ta



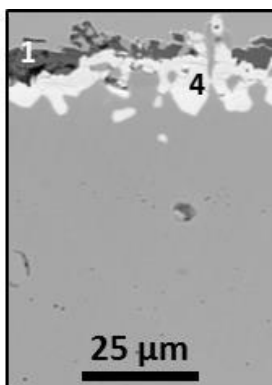
Co(bal.)/14.5Ni
25Cr-0.4C-6Ta



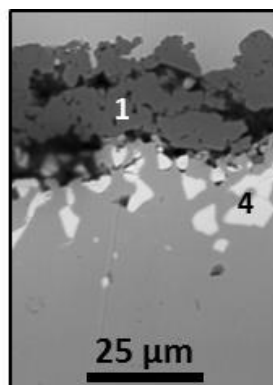
Co(bal.)/0 Ni
25Cr-0.4C-6Ta

1: Cr₂O₃, 2: CoCr₂O₄, 3: (Co,Ni)O or CoO, 4: CrTaO₄

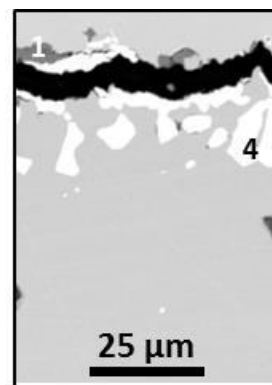
Figure 2; Cross-sectional observation of the oxidation results for the (Ni, xCo)-25Cr-0.4C-6Ta alloys oxidized at 1127°C for 24h.



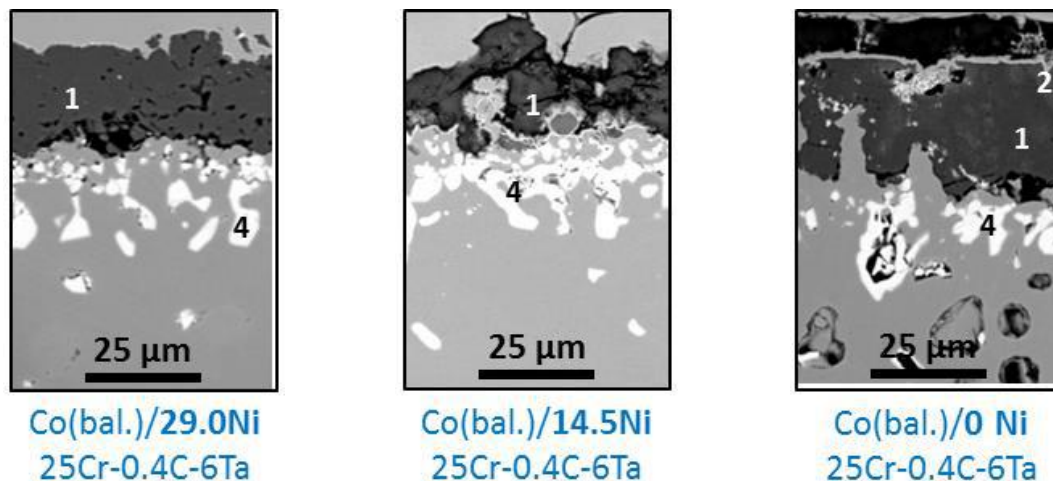
Ni(bal.)-0 Co
25Cr-0.4C-6Ta



Ni(bal.)/14.5 Co
25Cr-0.4C-6Ta



Ni(bal.)/29.0 Co
25Cr-0.4C-6Ta

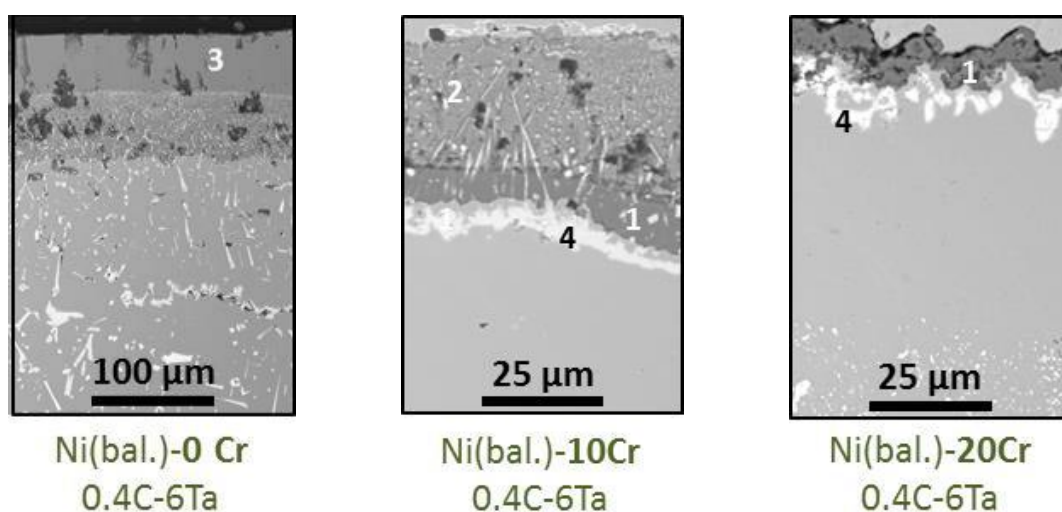


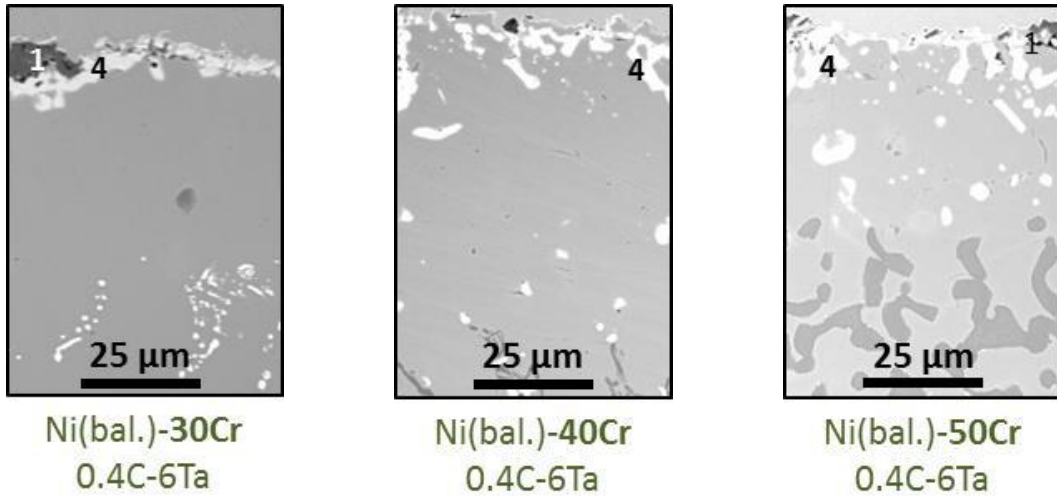
1: Cr₂O₃, 2: CoCr₂O₄, 3: (Co,Ni)O or CoO, 4: CrTaO₄

Figure 3; Cross-sectional observation of the oxidation results for the (Ni, xCo)-25Cr-0.4C-6Ta alloys oxidized at 1237°C for 24h.

3.3 The (Ni, 0 ≤ Cr ≤ 50)-0.4C-6Ta alloys oxidized at 1127°C and 1237°C

Figure 4 illustrates the oxidized states of the Ni-based alloys containing 0.5wt.%C and 6wt.%Ta and various concentrations in chromium, after exposure at 1127°C. In all cases where the Cr content is equal or higher than 20 wt.% (the threshold for nickel alloys for being chromia-forming) oxidation was seemingly limited. Because of the formation of CrTaO₄ at the alloy/oxide interface chromia was lost by spallation during cooling but some parts of external oxide remains here and there and all these parts are made of chromia. The alloy containing only 10wt.%Cr did not wholly act as chromia-forming alloy and the external oxide scale is very thick and composed of two distinct layers: an inner layer made of chromia and an outer layer composed of a complex oxide of both chromium and nickel. In total absence of chromium the concerned alloy was severely oxidized (100µm of oxides). The tantalum carbides were oxidized on place, keeping globally the same morphology, while NiO developed, seemingly inwards and outwards at the same time. Indeed there were seemingly a growth of NiO in the direction of the bulk, this part being evidenced/marked by the presence of the oxides of tantalum or of tantalum and nickel, and also a growth in the other direction leading to an oxide scale made of exclusively NiO. This is better illustrated in **Figure 5**. After 24 hours of oxidation at 1237°C the oxidation features are globally the same, with logically more extended degradation in thickness of depth (Figure 6).





1: Cr₂O₃, 2: complex oxide of Ni and Cr, 3: NiO, 4: CrTaO₄

Figure 4; Cross-sectional observation of the oxidation results for the (Ni, 0 ≤ Cr ≤ 50)-0.4C-6Ta alloys oxidized at 1127°C for 24h.

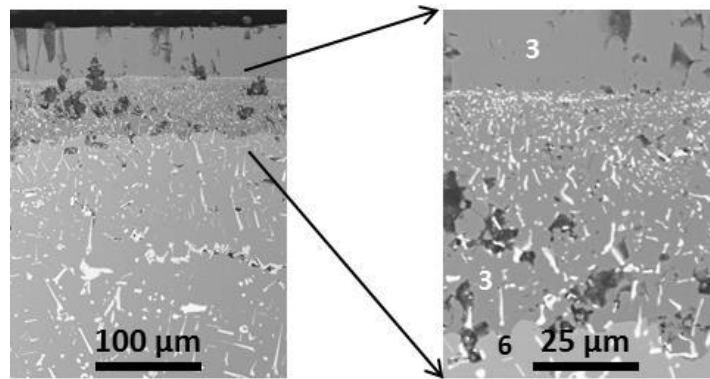
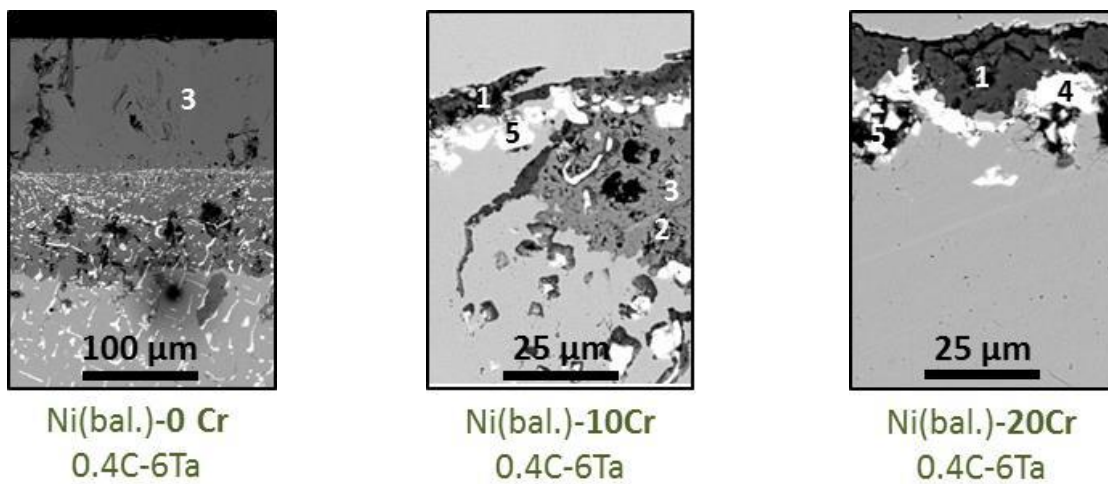


Figure 5; Cross-sectional observation of the oxidation results for the chromium-free Ni-0Cr-0.4C-6Ta alloy oxidized at 1127°C for 24h.



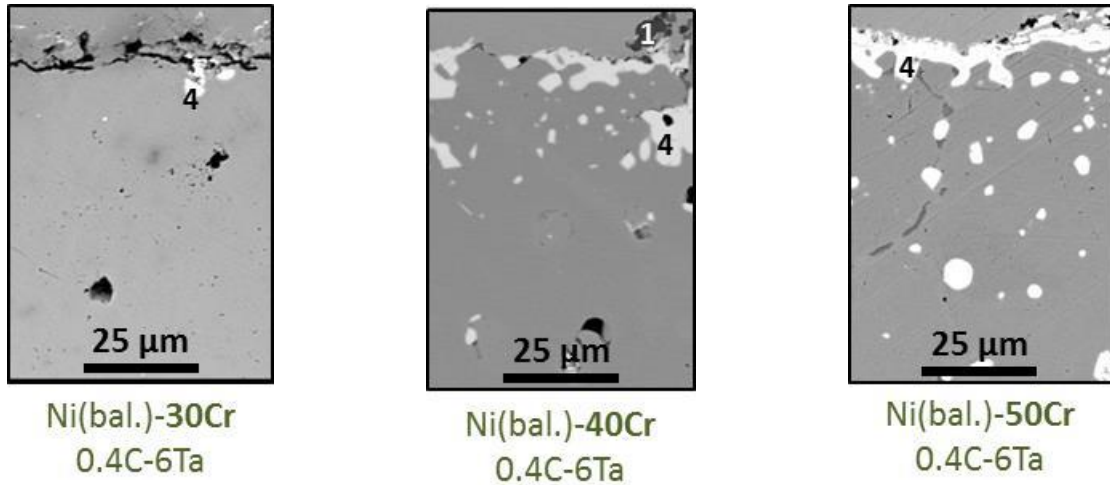
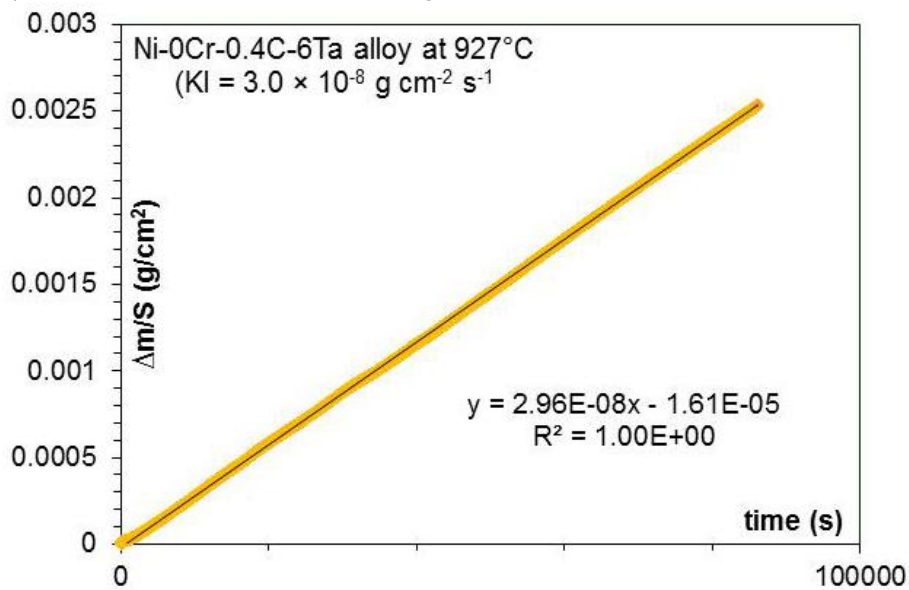


Figure 6; Cross-sectional observation of the oxidation results for the (Ni, 0 ≤ Cr ≤ 50)-0.4C-6Ta alloys oxidized at 1237°C for 24h.

3.4 Test of oxidation of the chromium-free Ni-0Cr-0.4C-6Ta alloys at lower temperatures

To complete the oxidation study of the Ni-0Cr-0.4C-6Ta alloy two thermogravimetric experiments were carried out using a thermo-balance in a flow of synthetic air. This was done for 24 hours at 927°C (i.e. 200°C less than 1127°C) and 827°C (300°C less). The obtained curves are shown in **Figure 7**.



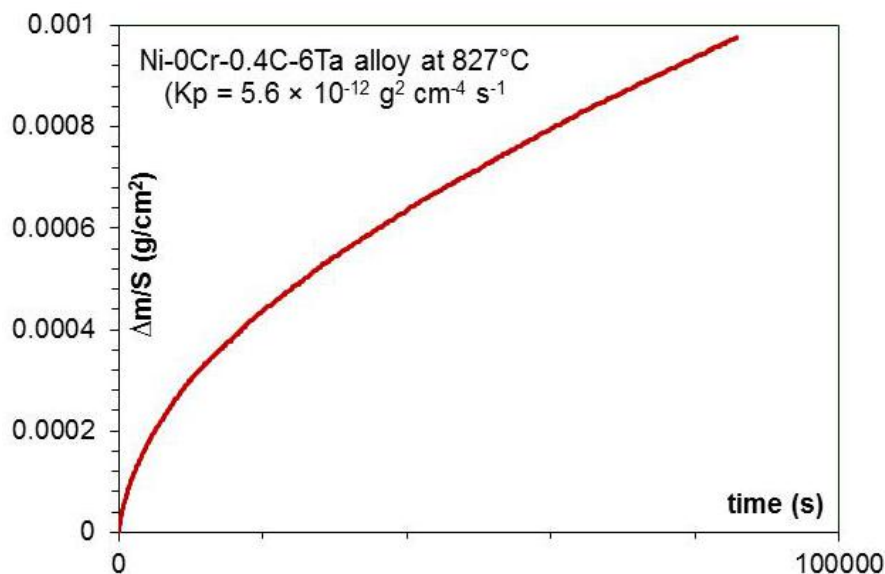


Figure 7; Thermogravimetric runs of oxidation performed for the chromium-free Ni-0Cr-0.4C-6Ta alloy at 927°C (top) and at 827°C (bottom).

In the first case (927°C) the mass gain was linear and rather fast (the linear constant K_l , equal to $3 \times 10^{-8} \text{ g cm}^{-2} \text{ s}^{-1}$, is of the same order of magnitude as the linear constant characterizing the possible transient oxidation preceding the Wagner's regime for a chromia-forming alloy isothermally studied at 1000°C). In the second case (827°C) the isothermal mass gain is parabolic (Wagner's regime). The parabolic constant K_p , equal to $6 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$, is the same as a chromia-forming alloy isothermally oxidized at 1000°C too). Thus, taking into account the rather low temperatures of these two thermogravimetric tests, one can consider that the absence of chromium is dramatic for this alloy. This confirms what can be thought when considering the previous metallographic observations for this alloy exposed at higher temperatures; even if tantalum is present in high quantity and is able to diffuse and constitute a rather important oxide population close to the surface this one cannot act as a barrier.

4. Conclusion

This oxidation study of the behavior of these three series of alloys confirmed that chromium is a key element for the oxidation resistance at high temperature. This is of course not new. What is maybe more interesting is the deleterious role of cobalt when added to a nickel-based alloys (or inversely the favorable role of nickel in a cobalt-based alloy), which make that the 25 wt.%Cr content can be considered as a sufficient chromium content or as not sufficient. 20wt.% is from long time cited as a critical threshold for nickel-based alloys while this is 30wt.% for cobalt alloys, without precision or conditions about the elaboration mode of these alloys or their metallurgy (solid solution strengthening principle, reinforcement by carbides or not ...). Here, in the specific case of equiaxed and polycrystalline alloys, of two types of MC carbides, of an interdendritic location of these hard particles ... one verified that the previously evocated rules (Cr threshold) are also applicable.

Author Contributions

PB, associate professor, has elaborated all alloys, achieved the main part of the sample preparations in their as-cast and their oxidized conditions. He has taken part to the SEM examinations, interpreted the results and written the manuscript. ZH, LT and OA are students of Master 1 and Master 2 in trainee period. ZH and OA learned how preparing metallographic samples and to use the SEM. They took an active part in the SEM examinations. OA (Master 2) and ML (Ph.D. in preparation) helped them by performing the thermogravimetry tests.

Conflict of Interest

There is no conflict of interest.

Acknowledgments

The authors wish to thank Dr. Pierre-Jean Panteix who helped them to use the furnace involved in the oxidation

runs.

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