

BEHAVIORS OF (Ti, C)-CONTAINING CAST (Co, Ni)-BASED SUPERALLOYS IN OXIDATION AND CREEP AT 1200°C

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Six alloys (25 wt% Cr, 0.4 C, 1.6 Ti, Co and Ni (bal.)) were prepared by casting for evaluating their oxidation and creep properties at 1200°C. Their microstructures consist of a dendritic matrix with eutectic carbides in the interdendritic spaces. Carbides are TiC for the alloys richer in Co than in Ni, and chromium carbides in the alloys richer in Ni than in Co. Differential thermal analysis shows that all alloys start melting above 1250°C. The oxidation tests in air at 1200°C allow observing a chromia-forming behavior of the alloys rich in nickel better than the cobalt alloys. In contrast, the creep resistance tests at 1200°C demonstrate an undeniable superiority of the alloys rich in cobalt. Good compromise for both types of high temperature behavior appears to be obtained by a Co-base alloy containing nickel as minor element but with significant proportion in nickel (15...30 wt% Ni).

Keywords: *Co and Ni alloys, TiC carbides, chromium carbides, creep resistance, high temperature oxidation.*

Шість сплавів (25 wt% Cr; 0,4 C; 1,6 Ti; решта – Co і Ni) виготовлено литтям для оцінки їхнього опору окисненню та повзучості при 1200°C. Мікроструктура сплавів складається з дендритної матриці з евтектичними карбідами у міждендритних проміжках. Карбіди TiC утворюються у сплавах з більшим вмістом Co, а карбіди хрому – з більшим вмістом Ni. Диференціальний термічний аналіз показує, що всі сплави починають плавитися за температури вище 1250°C. Окиснення на повітрі при 1200°C дає змогу спостерігати захисні властивості хрому на сплавах, збагачених нікелем, сильніші, ніж кобальтом. І, навпаки, випробування на повзучість при 1200°C демонструють беззаперечну перевагу багатших на кобальт сплавів. Хорошим компромісом для обох типів поведінки за високих температур є сплав на основі кобальту з нікелем як другорядним елементом, але з великою часткою (15...30 wt% Ni).

Ключові слова: *сплави Co та Ni, карбіди TiC, карбіди хрому, опір повзучості, високотемпературне окиснення.*

Introduction. Many conventionally cast superalloys contain simultaneously cobalt and nickel to constitute their matrix. For a given chromium content the Co/Ni balance can influence significantly the oxidation resistance at high temperature [1]. In another way, the addition of titanium to alloys which are first rich in chromium for the purpose of chemical resistance at high temperature, and second which contain carbon for the formation of strengthening carbides, can modify the characteristics of the carbides population. This effect, due to the strong carbide-forming behavior of this element [2], may influence the mechanical properties of the whole alloy at a high temperature [3–5]. Ti may also significantly influence the high temperature oxidation behavior for (Co, Ni)-based alloys and others [6, 7]. The introduction of 1 or 2 wt% Ti to chromium-rich alloys based on cobalt, have been recently tested and it is observed that titanium monocarbides precipitate during solidification instead of the chromium carbides that are obtained usually in (Co–25...30 wt% Cr–0.25...0.5 wt% C) alloys [8].

When such alloys are exposed for a long time to high temperature (1000...1200°C) they tend to keep a significant part of their initial TiC carbides, notably when the alloy initially contains a high fraction of TiC (0.5 wt% C; 2 wt% Ti) or when temperature is not too high (1000°C) according to thermodynamic calculations [9].

Alloys based on cobalt and chromium only are likely to be affected by possible allotropic changes of the crystalline network of their matrix in some conditions of heating or cooling, with possible deleterious effects on their internal stress state. Usually to limit these problems, nickel is often added to avoid such solid state transformation in thermal cycling conditions [10], by helping the austenite stabilization [11]. In the case of cobalt-based alloys designed to be strengthened by titanium carbides, such nickel addition, useful for the crystalline stability, may also influence the alloy carbides population, the mechanical resistance at elevated temperature and the hot oxidation behavior. The present work aims to explore these possible effects on the quantity of nickel added to the composition by elaborating alloys derived from a reference cobalt alloy and by the characterization of their properties.

Method of investigation. A series of six alloys all containing 25 wt% Cr, 1.6 Ti and 0.4 C were considered: first the reference Ni-free Co-based alloy and two versions with a moderate Ni addition. Another alloy with more Ni and three Ni-rich alloys were also elaborated to push the study further to an alloy based on nickel and without any cobalt. The names and chemical compositions of the six alloys are given in Table 1. 40 g of each of the six alloys were produced from pure elements (Alfa Aesar, > 99.9 wt%) in the water-cooled copper crucible of a high frequency induction furnace under 300 mbars of pure Ar. Four types of samples were extracted from each of the obtained ingots, by cutting. The first compact one was kept for the metallographic study of the as-cast microstructure. The small second one was reserved for performing differential thermal analysis (DTA) to specify the melting start temperature of the alloy. A third one, a square-based parallelepiped, was destined to oxidation test in a furnace. To finish, the fourth one, an elongated parallelepiped, was prepared for performing a creep bending test.

Table 1. Designation and chemical compositions of the six studied alloys

Co-rich alloys	Ni	Cr	Ti	C
	wt%			
5Co0NiTi	0	25	1.6	0.4
4Co1NiTi	15	25	1.6	0.4
3Co2NiTi	29	25	1.6	0.4
Ni-rich alloys	Co	Cr	Ti	C
	wt%			
0Co5NiTi	0	25	1.6	0.4
1Co4NiTi	15	25	1.6	0.4
2Co3NiTi	29	25	1.6	0.4

The metallographic samples were embedded in cold resin and ground with 250 to 1200-grit SiC papers. This was followed by polishing using 1 µm hard particles for obtaining a mirror-like state. They were examined using a scanning electron microscope (SEM, JEOL JSM6010LA). The observations were carried out under 20 kV in the back scattered electrons (BSE) mode, at various magnifications (from 125 to 1000). The ob-

tained chemical compositions were measured using the energy dispersive spectrometry (EDS) device present in the SEM.

The 7×2×2 mm DTA sample was heated up to 1500°C and cooled, with recording of the heat flow to plot it versus temperature. The temperatures of melting start and end, and of solidification start and end were noted to specify the solidus and liquidus temperatures. The dimensions of the samples for the hot oxidation tests were 8×8×3 mm and these samples, ground all around with 1200-grit SiC paper, were exposed for 170 h to laboratory air at 1200°C. The oxidized samples, after return to room temperature, were embedded and cut to obtain cross-sectional samples. These ones were thereafter ground, polished, observed and analyzed as the as-cast metallographic samples, however with special attention to the oxides formed externally and internally. The creep samples with dimensions 1×2×15 mm were ground with 1200-grit SiC paper with final strips in the length direction. They were subjected for 70 h at 1200°C to a constant central load calculated to induce a tensile stress of 7.5 MPa in the bottom center of the parallelepiped.

Results and discussion. The EDS analyses show that the targeted chemical compositions have been successfully obtained. The microstructures of the six alloys in the as-cast condition are illustrated in Fig. 1. The six SEM/BSE micrographs show that the matrix of all alloys is dendritic and more or less dark particles are present in the interdendritic spaces. The EDS spot analyses carried out on the coarsest particles of each type demonstrate that the black ones are TiC particles. These ones are Chinese script shaped in the 5Co0NiTi and 4Co1NiTi alloys, are of elongated shape in the 3Co2NiTi one, and are small blocky in the 2Co3NiTi one). The grey ones are coarse Cr₂₃C₆ in the 3Co2NiTi alloy and Cr₇C₃ in the 2Co3NiTi, 1Co4NiTi and 0Co5NiTi alloys. So, as previously observed in the case of TaC carbides, more Ni and less Co disadvantage monocarbides and promote chromium carbides in an environment with 25...30 wt% Cr.

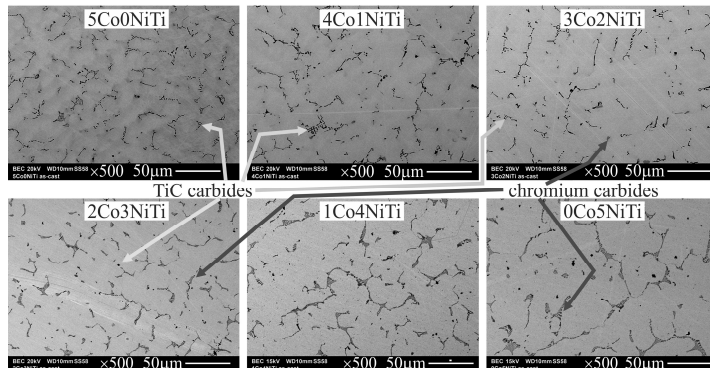


Fig. 1. Microstructures of the as-cast six alloys with arrows designating TiC and Cr carbides.

The DTA runs performed for the six alloys allow specifying the temperatures of melting start and melting end in the heating part, and the temperatures of solidification start and solidification end in the cooling part. The average of the temperatures of melting end and solidification start is calculated (evaluation of the liquidus temperature), as well as the one of the temperatures of melting start and solidification end (solidus temperature). All these results are graphically presented in Fig. 2. Globally, the liquidus temperature increases with the cobalt content, while the evolution is not monotonous for the solidus temperature (minimal values for equivalent contents in Ni and in Co). One can notice that all temperatures related to the solidus are above 1250°C. This leads to the choice of 1200°C for the oxidation and creep tests, the highest temperature which remains however reasonably far from all solidus.

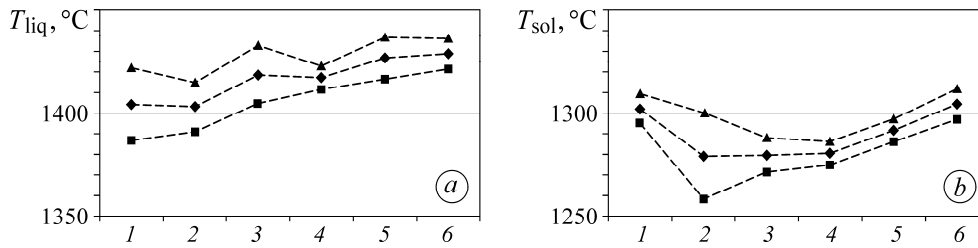


Fig. 2. Temperatures of liquidus (*a*: ▲ – melting end, ◆ – average, ■ – solidification start) and solidus (*b*: ▲ – melting start, ◆ – average, ■ – solidification end) for the six alloys, according to the results of the DTA:
 1 – 0Co5NiTi (0% Co, 73% Ni); 2 – 1Co4NiTi (15% Co, 58% Ni);
 3 – 2Co3NiTi (29% Co, 44% Ni); 4 – 3Co2NiTi (44% Co, 29% Ni);
 5 – 4Co1NiTi (58% Co, 15% Ni); 6 – 5Co0NiTi (73% Co, 0% Ni).

After 170 h spent in laboratory air at 1200°C in the muffle furnace six alloys were covered by an external oxide scale. The SEM/BSE observations (Figs. 3 and 4) and the EDS spot analyses carried out on the prepared cross-sections allow distinguishing a double constitution of the external scale in the case of the three Ni-based alloys (from 2Co3NiTi to 0Co5NiTi): they are covered by a thick continuous chromia scale, which is itself covered by an outermost thin continuous TiO₂ layer. The 3Co2NiTi and 4Co1NiTi alloys are covered by an oxide scale made of chromia only (no outermost TiO₂ layer, seemingly). For the nickel-free Co-based alloy (5Co0NiTi), chromia was present as a discontinuous inner layer more or less penetrated in the alloy. This chromia layer was covered by a thick external scale constituted by a mix of cobalt oxide (CoO) and of spinel oxide (CoCr₂O₄). Internal oxidation also occurred, with the appearance of finely dispersed TiCr₂O₄ oxides in the subsurface close to the alloy/scale interface, and of coarse internal Cr₂O₃ oxides. The thicknesses of the external scales are summarized in Table 2. Clearly, adding Ni to the reference Co-rich alloy improves significantly the oxidation resistance by promoting the development of protecting chromia. The Ni-free 5Co0NiTi alloy was the single alloy concerned by start of generalized oxidation (particularly thick oxide scale). To finish, one can mention that, in the case of the chromia-forming alloys, the chromia scale is obviously preserved from volatilization by the outermost TiO₂ scale. Indeed, the chromia scale is slightly thicker for the Ni-rich alloys. This is an effect of TiO₂ which was earlier observed.

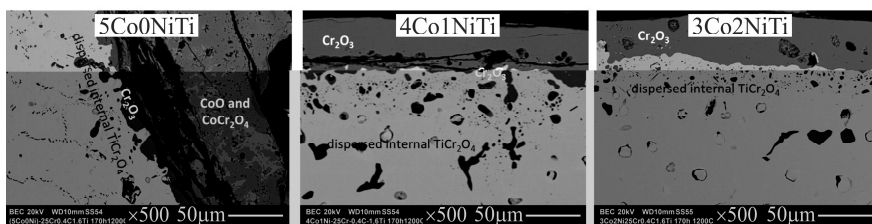


Fig. 3. Surface of the three Co-rich alloys states after 170 h at 1200°C.

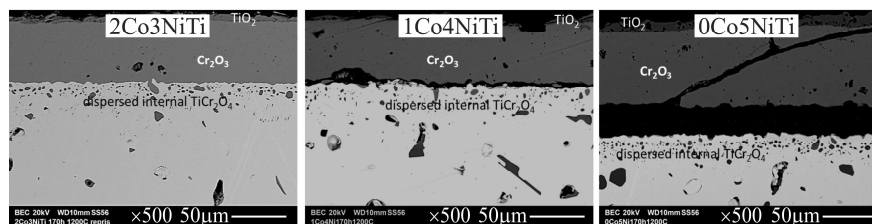


Fig. 4. Surface of the three Ni-rich alloys states after 170 h at 1200°C.

Table 2. Oxides and their thickness observed on the surfaces and in the subsurfaces

Co-rich alloys	External scale	Internal oxides	Ext. ox. thickness
5Co0NiTi (73% Co, 0% Ni)	Cr ₂ O ₃ , TiO ₂ , CoCr ₂ O ₄ , CoO	TiO ₂ , TiCr ₂ O ₄ , Cr ₂ O ₃	120 μm
4Co1NiTi (58% Co, 15% Ni)	Cr ₂ O ₃ , TiO ₂	TiO ₂ , TiCr ₂ O ₄ , Cr ₂ O ₃	40 μm
3Co2NiTi (44% Co, 29% Ni)	Cr ₂ O ₃ , TiO ₂	TiO ₂ , TiCr ₂ O ₄ , Cr ₂ O ₃	40 μm
Ni-rich alloys	External scale	Internal oxides	Ext. ox. thickness
0Co5NiTi (0% Co, 73% Ni)	Cr ₂ O ₃ , TiO ₂	TiO ₂ , TiCr ₂ O ₄ , Cr ₂ O ₃	70 μm
1Co4NiTi (15% Co, 58% Ni)	Cr ₂ O ₃ , TiO ₂	TiO ₂ , TiCr ₂ O ₄ , Cr ₂ O ₃	60 μm
2Co3NiTi (29% Co, 44% Ni)	Cr ₂ O ₃ , TiO ₂	TiO ₂ , TiCr ₂ O ₄ , Cr ₂ O ₃	60 μm

The center of each oxidized sample is also observed. After 100 h at 1200°C the microstructures are all considerably modified (Fig. 5). The TiC carbides (5Co0NiTi and 4Co1NiTi alloys), the chromium carbides (1Co4NiTi and 0Co5NiTi) and both of them (3Co2NiTi and 2Co3NiTi) become rounder and coarser (coalescence). The TiC have completely lost their initial Chinese script or elongated shapes while the geometry of the chromium carbides has evolved from acicular to round. This shape evolution may be deleterious for the creep resistance.

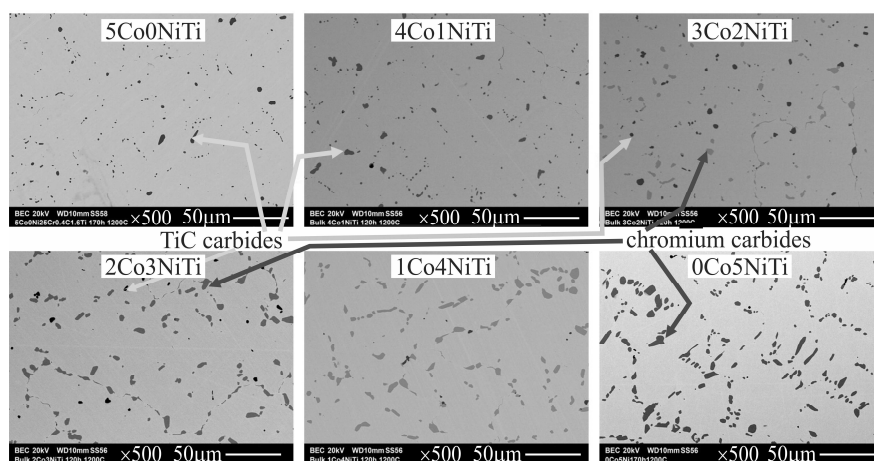


Fig. 5. Aged microstructures of six alloys with arrows designating TiC and Cr carbides.

The specimens for the three-point bending creep tests are loaded in the center of their upper side in order to induce and maintain a constant tensile stress equal to 7.5 MPa in the center of their bottom face. The obtained creep curves (downward movement of the upper central point) are shown in Fig. 6. All curves present an initial fast deformation which decelerates at a constant rate of deformation after 10 h (5 h in some cases). Six values of total movement of the central point achieved at 70 h of test and the stabilized deformation rate (counted at $t = 70$ h too) are measured and the values are displayed in Table 3. Obviously, the best resistant alloys against creep are three cobalt-rich alloys. Adding more nickel to the (Ni = Co) equivalence progressively

lowers this resistance. The less creep-resistant alloy is the cobalt-free Ni-based one, but, seemingly, adding nickel in moderate amounts does not threaten its creep strength. However it seems that Ni must never be more present than cobalt to avoid the weakening of the alloy seen for the 2Co3NiTi, 1Co4NiTi and notably 0Co5NiTi alloys.

Fig. 6. The creep deformation curves for six alloys (3-point bending, 7.5 MPa, 1200°C):
1 – 0Co5NiTi; 2 – 1Co4NiTi;
3 – 2Co3NiTi; 4 – 3Co2NiTi;
5 – 4Co1NiTi; 6 – 5Co0NiTi.

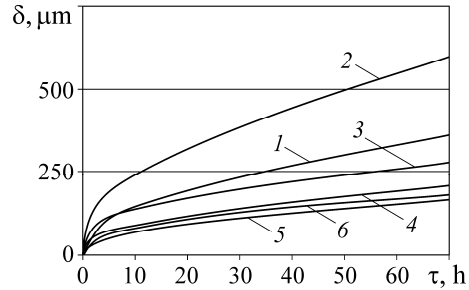


Table 3. Oxide species observed over the samples surfaces and in the subsurfaces

Co-rich alloys at 70 h-creep	Central point position, μm	Central point movement final speed, $\mu\text{m/h}$
5Co0NiTi (73% Co, 0% Ni)	180	1.18
4Co1NiTi (58% Co, 15% Ni)	166	1.11
3Co2NiTi (44% Co, 29% Ni)	208	1.67
Ni-rich alloys at 70 h-creep	Central point position, μm	Central point movement final speed, $\mu\text{m/h}$
0Co5NiTi (0% Co, 73% Ni)	363	3.31
1Co4NiTi (15% Co, 58% Ni)	599	4.89
2Co3NiTi (29% Co, 44% Ni)	277	1.82

CONCLUSIONS

The alloys based on cobalt, containing several tens wt% of chromium and designed to be strengthened by eutectic TiC carbides with a Chinese script shape are of great interest, even with their rather simple chemical composition in comparison with industrial superalloys. Even at a temperature particularly high (1200°C) for alloys of such category (conventionally cast, not precipitation-strengthened) the general behavior is obviously good. There is reasonable resistance against oxidation but superior creep-resistance. The oxidation resistance is enhanced with moderate addition of nickel as demonstrated by the 4Co1NiTi and 3Co2NiTi alloys, for which the high creep resistance is fortunately maintained. So, much cobalt and 15 wt% of nickel (or a little more) may lead to interesting and exploitable properties in the mechanical and chemical field at this elevated temperature. A base element shared between 4/5 to 3/5 of Co and 1/5 to 2/5 of Ni (i.e. 4Co1NiTi and 3Co2NiTi and intermediate alloys) is a design which appear to be advised.

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