Materials Chemistry and Physics 212 (2018) 260–267

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

# Dependence of titanium carbide stability at elevated temperatures on Co content in Co(Ni)-25Cr-1.6Ti-0.4C superalloys

Patrice Berthod*, Lydia Toubal

*Institut Jean Lamour, Department N°2: Chemistry and Physic of Solids and Surfaces, Team "Surface and Interface, Chemical Reactivity of Materials", Faculty of Sciences and Technologies, University of Lorraine, B.P. 70239, 54506 Vandoeuvre-lès-Nancy, France*

## HIGHLIGHTS

- Six Ni alloys with 25Cr, 0.4C, 1.6Ti and varying Co content were elaborated.
- The as-cast microstructures contain chromium carbides and/or TiC.
- The addition of Co progressively stabilizes the TiC at high temperature.
- The hardness is more governed by the matrix chemical composition than by carbides.
- The high temperature oxidation behavior is deteriorated by the Co addition.

## ARTICLE INFO

*Article history:*
Available online 20 March 2018

*Keywords:*
Alloys
Solidification
Electron microscopy
Hardness
Oxidation

## ABSTRACT

Titanium carbides feature among the MC carbides which tend to crystallize with a script-like shape recognized to be favorable to mechanical strength at high temperature for equi-axed cast refractory alloys. Recent results demonstrated that script-like TiC can be successfully obtained in Co-based alloys while they are less stable than chromium carbides in nickel-based alloys. The present work aims to study whether the addition of cobalt to nickel-based alloys may stabilize TiC. This double investigation, by thermodynamic calculations and by the elaboration of a series of nickel-based alloys with an increasing part of cobalt, demonstrates that the progressive enrichment in cobalt tends favoring the presence of TiC instead chromium carbides. To obtain a majority of TiC, script-like shaped and in significant quantity, cobalt must be more present than nickel in the alloys. But this enrichment in cobalt deteriorates the good resistance against hot oxidation.

## 1. Introduction

The increase of needs in alloys offering high refractoriness, high temperature mechanical resistance, hot oxidation and corrosion resistance and possible manufacturability in complex shapes induces the maintenance of interest of the classical principle of equi-axed polycrystalline superalloys existing since several decades [1,2]. Some recent evolutions of chemical compositions allowing both high solidus temperature and good stability of the interdendritic strengthening particles such as MC carbides [3,4]. Beside the classical tantalum carbides or the maybe more innovative hafnium carbides, another MC carbide type, the TiC one, presents great potential interest thanks to the better availability of the involved metallic element. Titanium is a light metallic element, used for example for aeronautic components possibly exposed to moderate and even high temperatures (as aluminides [1,2]) or in biomedical applications [5,6]. It is a strong carbide-former element, as well as a nitride-former one, this allowing it to be involved in bulk materials as well as in coatings, to improve the room or high temperature mechanical behaviour of various components [7–9]. In these applications titanium is often associated to other MC-former elements as Nb or W, this leading to multimetallic MC carbides not necessarily very stable at high temperature [10–12].

In conventionally cast alloys, the presence of titanium together with carbon in equal atomic quantities allows obtaining, in some alloys, microstructures with interdendritic TiC as single carbide present, even in presence of high amount of another carbide-former element, chromium, added for combatting high temperature oxidation and corrosion [13,14]. This was observed, for

---

* Corresponding author.
*E-mail address:* patrice.berthod@centraliens-lille.org (P. Berthod).

https://doi.org/10.1016/j.matchemphys.2018.03.061
0254-0584/© 2018 Elsevier B.V. All rights reserved.

example, in the case of 25 wt%Cr-containing cobalt-based conventionally cast alloys [15].

But there are seemingly other cases for which TiC can be less stable than chromium carbides. For similar contents in all the other elements, titanium carbides are much less present than chromium carbides in as-cast nickel-chromium alloys, despite the atomic equivalence between Ti and C [16]. Furthermore, exposures to high temperature may lead to the total disappearance of the rare TiC initially present in the as-cast state.

Thus, in the family of the high temperature cast alloys based on cobalt or nickel, rich in chromium, containing titanium and carbon, and the strengthening principle of which is based on interdendritic carbides, one have:

- on the one hand the low chemically resistant but potentially strongly mechanically resistant TiC-reinforced cobalt-based alloys
- on the other hand the good chemically resistant but less efficiently resistant chromium-carbides nickel-based alloys.

After having observed that TiC carbides successfully precipitate at solidification in cobalt-based alloys even in presence of large amount in chromium, with, in addition, a good stability during exposures at high temperature, and all the contrary for chromium-containing nickel-based alloys, one thought that some alloys containing simultaneously cobalt and nickel as base elements may present an intermediate microstructure behaviour, and why not a dense interdendritic TiC network in a nickel-based alloys thanks to the presence of a not too high amount in cobalt. Such possible result could lead to alloys presenting, at high temperature, both correct high temperature mechanical strength and good oxidation and corrosion resistance. This is what is investigated in the present work, by synthesizing a series of {25Cr, 0.4C and 1.6Ti, wt.%}-containing alloys with varying Co/Ni ratio, observing their as-cast microstructures and exploring their microstructural and surface stabilities during an isothermal exposure at a chosen high temperature and in an oxidative atmosphere.

## 2. Material and methods

### 2.1. Selection the alloys

For this study six chemical compositions of alloys were chosen. First, the chromium content was fixed at 25 wt%Cr, which can be taken as a minimal value to hope remaining chromia-forming for nickel and cobalt-based alloys. Second the content in carbon was fixed at 0.4 wt%, which is known as being a value that allows obtaining an interdendritic carbide network (whatever the carbides' natures) dense enough to efficiently strengthen such alloys but not too developed to become interconnected and then to threaten the impact toughness/crack propagation of the alloys. Third, the Co and Ni contents were chosen for targeting the 0, 1, 2, 3, 4 and 5 values of the Co/(Ni + Co) weight content ratio. The corresponding alloys are logically named “Ni5Co” (Ni-based), “Ni4Co1”, “Ni3Co2”, “Ni2Co3”, “Ni1Co4” and “Ni0Co5” (Co-based). This repartition allows exploring uniformly the microstructure evolution gradually as the Co content increases.

### 2.2. Thermodynamic calculations

Predictive thermodynamic calculations were, prior to real experiments, carried out to anticipate the microstructures corresponding to theses chemical compositions. They were done using the Thermo-Calc software [17] and the SSOL database [18] enriched with additional thermodynamic data. The obtained database contains the description of many binary and ternary systems. Among them are the following Ti-containing ones: Ti-C, Ti-Ni, Ti-Co, Ti-Cr, Ti-Co-C and Ti-Cr-C.

### 2.3. Elaboration

The six alloys were synthesized by high frequency induction (about 100kHz) melting. The charges of pure elements (Ni, Co, Cr, Ti: purity > 99.9%, Alfa Aesar; C: pure graphite) were prepared to obtain 40 g of alloy in case. Each charge was put in the copper crucible of a CELES furnace and a silica tube was placed around to isolate the fusion chamber from laboratory air. Pumping was applied until reaching about $7 \times 10^{-2}$ mbars, just before the injection of 800 mbars of pure argon. This cycle was thereafter applied two times again, before filling the chamber with pure argon for a final internal Ar pressure of about 200 mbars.

Heating was progressively performed, until 2.5 kV in a first time. After apparent thermal homogenization of the parts of the pure elements, the voltage was increased again to reach 4 kV. After about 5 min of chemical homogenization in the liquid state, the applied power was progressively decreased. The alloys solidified (during about 1 min), then cooled in solid state. Their temperature reached the ambient one after about half an hour. The obtained ingots, compact-shaped, were thereafter cut in several parts for the characterization of their as-cast microstructures and for carrying out the exposures at high temperature.

### 2.4. Exposure to high temperature and handling of the aged/oxidized samples

After cutting with a metallographic saw (Abrasimet 5000 Delta Buehler), a quarter of each ingot was taken. These six parts were ground all around using 1200-grit SiC papers. They were placed in a Nabertherm muffle furnace, in which they were heated until reaching 1400 K, temperature at which they were maintained during 20 h before cooling. The aged samples were carefully handled to limit possible loss of the external oxide scale. A cathodic gold deposition was realized on their surface to get the outside electrical conductivity compulsory for the subsequent electrolytic nickel deposition. This later operation was carried out in a Watt's bath heated at 50 °C, with an operating parameters: 1.6 $A/dm^2$ and 2 h. The samples, cathodically polarized (anodes: pure nickel coupons), were thus covered by a nickel coating thick enough to protect the external scales during the subsequent cutting leading to two halves allowing the preparation of samples for metallographic observation and indentation.

### 2.5. Metallographic characterization

For each alloy, the part kept for the as-cast microstructure observation and the one issued from aging, Au then Ni coatings and cross-sectional cutting, were embedded in a cold resin mixture. After total resin stiffening the samples were ground with successive SiC papers from #250 to #1200, ultrasonically cleaned, then finished using a textile disk enriched with 1 μm hard particles. The obtained mirror-like state allowed metallographic observations by electron microscopy. This was done using a JEOL JSM-6010LA scanning electron microscope (SEM), with an acceleration voltage equal to 20 kV. The Energy Dispersive Spectrometry attached to the SEM was used to control the general chemical composition of the alloys (full frame analysis at × 250), to identify the different observed phases (alloy) and oxides (internal ones and external scale), by spot analysis at × 1000), and to specify the chemical changes in the outer part of the aged alloys, notably by acquiring concentrations profiles.