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Experimental and thermodynamic investigations regarding the effect of chromium on the carbides population in cast {Ni(bal.)-0.4C-6Ta-xCr} alloys with x varying from 0 to 50 wt%

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ABSTRACT

Involving a particularly strong carbide-former metallic element, the tantalum carbides are potentially very stable at elevated temperatures in term of volume fraction and morphology. The TaC phase represents a major strengthening way to allow cast chromium-rich superalloys resisting mechanical stresses at elevated temperatures. They are exploited in recent high performance cobalt-based superalloys but seemingly not in nickel-chromium refractory alloys. Earlier studies showed that the stability of TaC in Ni-Cr alloys is not so good as in the Co-Cr ones, and they evidenced that chromium carbides may compete with TaC in the formation of the carbides population. A possible way to optimize the presence of TaC in Ni-Cr alloy may consist in rating the chromium content to an ideal value but preliminary knowledge about the TaC dependence on the Cr content is compulsory. The aim of this work is precisely the investigation of the effect of the content in chromium on the appearance and stability of the TaC phase in Ni-Cr alloys, by the means of thermodynamic calculations and real experiments in parallel. A global system Ni(bal.)-xCr-0.4C-6Ta compositions (with x varying from 0 to 50 wt%) was chosen. Thermodynamic calculations were performed to know the theoretic metallurgical states inside the considered x range. These theoretic results being dependent on the suitability of the used database, real experiments of verifications were also carried out for a selection of six alloys (x = 0, 10, 20, 30, 40 and 50 wt%). The alloys prepared by respecting these compositions were cast and isothermally exposed at high temperature (1400 and 1510 K), then subjected to metallographic characterization. For the used database the calculated results showed that no TaC should never appear whatever their Cr content, while TaC were really observed in the as-cast and aged versions of the alloys containing 20 wt%Cr and more, but never alone since chromium carbides were systematically also present. When the Cr content in the alloy is too low, the TaC are rare or even no present. This allowed concluding first that the database used for the calculations needs serious improvements, followed by tests with, as first criteria of quality, a good correspondence with the present experimental results. Second, the presence of Cr in quantity high enough is surprisingly compulsory to obtain TaC carbides in quantity high enough, but it is no possible to avoid the appearance of chromium carbides. Obviously, other ways than Cr adjustments must be found to obtain TaC in nickel-based alloys as the single carbide phase and in quantity high enough to achieve high mechanical properties at high temperature.

1. Introduction

The superalloys with superior high temperature mechanical and oxidation properties are still the γ'-reinforced and alumina-forming Ni-based single crystals [1,2], together with Oxide Dispersion Strengthened (ODS) superalloys [3,4]. However new refractory alloys, such as the alloys based on niobium [5,6] or the ones consisting in MAX phases [7,8] for instance, are currently emerging and will perhaps compete with the γ/γ'-single crystalline superalloys in a next future. But the more traditional chromia-forming superalloys elaborated by conventional casting remain interesting for some specific high temperature applications (e.g. inducing contact with molten aggressive substances [9]) and for geometrically complex-shape pieces [10]. Among them one can find, from about 25 years, chromium-rich polycrystalline cobalt-based superalloys constituted of a dendritic matrix and of an interdendritic carbides skeleton exclusively made of eutectic tantalum carbides (TaC). They are designed for containing a developed enough (for efficient strengthening at high temperature) but not continuous carbide

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network (to preserve toughness at all temperatures), by rating the carbon content to about 0.4 wt%C and by adapting the Ta content to the C content (molar equivalence between Ta and C) to obtain only TaC carbides (i.e. without additional chromium carbides). These cobalt alloys are particularly performing at temperatures as high as 1200 °C [11] thanks to the good stability of the TaC carbides at elevated temperature [12,13]. Good TaC stability at high temperature was also met in chromium-rich iron-based [14] and iron/nickel-based [15] alloys, but TaC is unfortunately not so stable in hot conditions in chromium-containing nickel-based alloys [16]. Nickel-chromium alloys are known to be particularly resistant against high temperature oxidation and corrosion thanks to the easier volume diffusion of Cr across the Ni-based matrix, by comparison with the Co-based alloys for instance. This allows an efficient feeding in Cr of the oxidation front and thus a rapid development of the protective chromia scale and its maintenance for long time. Obtaining in addition an efficient strengthening carbides network made of exclusively TaC may lead to very interesting nickel-based alloys for high temperature applications involving creep, oxidation and corrosion phenomena.

Obviously, in the specific metallurgical context of nickel-chromium alloys, in contrast with what can be expected by considering the formation free enthalpies of TaC and of the Cr_7C_3 chromium carbide [17], carbon is not wholly involved in the formation of TaC but it is shared between Ta and Cr for forming the two types of carbides. One can imagine that, for fixed values of contents in C and Ta, varying the content in Cr, element which obviously competes with Ta, may change the TaC/Cr_7C_3 ratio. Exploring the effect of Cr variations on the respective proportions in TaC and Cr_7C_3 carbides will allow identifying ways to promote TaC at the detriment of chromium carbides. This is precisely this dependence on the chromium content of the nature of the carbide population which was investigated in this work, by involving both thermodynamic calculations and elaboration/characterization of real alloys. For that the chemical compositions of interest in this study were all derived from the Ni(bal.)-30Cr-0.4C-6Ta (wt%) one. This base composition is defined as follows: 30 wt%Cr for high resistance against hot oxidation and corrosion, 0.4 wt%C for an optimized strengthening effect of the interdendritic carbides, 6 wt%Ta (i.e. the same molar fraction as C) to allow obtaining, if possible, only TaC carbides. A preliminary exploration of the Ni(bal.)-xCr-0.4C-6Ta will be done for x ranging from 0 to 50 wt%. Thereafter, around 30 wt%, lower contents and higher contents in Cr were considered by slices of 10 wt% for the series of alloys to study by thermodynamic calculations again, and also to elaborate and to expose to high temperature and finally to metallographically characterize. By these means it is expected to establish the wished knowledge concerning the dependence of the nature of the carbides on the chromium content.

2. Experimental method

2.1. Choice of the chromium contents

In a first time this is the [0; 50] range of chromium content (wt%) (at the detriment of nickel) which was considered, for the calculation of the {0.4 C – 6Ta}-isopleth section of the Ni-Cr-Ta-C diagram. In a second time several chromium contents were chosen for obtaining quantitative calculated results; one decided to fix the Cr content to the following values:

- 30 wt%Cr as often used for the nickel-based and cobalt-based alloys devoted to high temperature service in oxidative/corrosive milieus (gases, melts…),
- Below the previous content: 20, 10 and even 0 wt% Cr,
- Above: 40 and even 50 wt%.

2.2. Thermodynamic calculations

The thermodynamic calculations were all carried out using the version N of the Thermo-Calc software [18]. Thermo-Calc worked using the thermo-data present in the SSOL database [19] which was later enriched by Michon [20] with the following additional systems: Co-Ta [21], Ni-Ta [22], Cr-Ta [23], Ta-C [24], C-Co-Ta [25], C-Ni-Ta [26] and Cr-Ni-Ta [27]. This allowed to qualitatively anticipate the possible microstructures of the alloys. The thermodynamic equilibria at 1400 K and 1510 K were computed to access to the mass fractions of the existing phases and of their chemical compositions.

2.3. Synthesis of the real alloys

The six alloys corresponding to the six chosen Cr contents were synthesized by casting using a CELES high frequency induction furnace. In each case a starting metallic mix composed of pure elements (purity of 99.99%, Alfa Aesar) was prepared. Each set was placed in a segmented copper crucible. First a silica tube was placed around, then a copper coil devoted to induce Foucault's electrical currents to heat metals by Joule's effect. The fusion chamber was then closed and the internal atmosphere (laboratory air) was replaced by a new one composed of pure argon (300 millibars). A 110 kHz/5 kV alternative current was progressively applied to the coil, using a generator. This induced the solid state heating of the different present metals, melting, alloying and chemical homogenization (duration of the stage: 3 min). The injected power was thereafter progressively decreased until solidification and solid state cooling. Without waiting room temperature, the power was increased again to perform, a second time, the same thermal cycle. During the heating, melting, isothermal stage, solidification and solid state cooling down to room temperature the crucible and the coil were permanently cooled by water circulation to avoid their heating and possible start of local melting. After half an hour of total cooling the obtained compact ingot was extracted from the furnace. All the obtained ingots were similar to cones, the sizes of which were all 20 mm in height and 20 mm in diameter.

2.4. High temperature exposures and metallographic preparation

Parts were machined in each ingot to obtain a sample for the as-cast microstructure observation, and two other ones devoted to high temperature exposures. These exposures were performed in a Nabertherm resistive furnace, at two levels of temperature: 1400 K and 1510 K. The isothermal stage duration was 24 h.

For a given alloy, the sample for the as-cast microstructure examination and the two samples aged at high temperature were cut in two parts and embedded in an Araldite resin. After total stiffening of the resin the embedded samples were extracted from the plastic molds. They were first ground with SiC papers from 240 to 1200-grit, cleaned by ultrasounds in water, then polished with textile enriched with 1 µm hard particles. The obtained mirror-like states were suitable for microscopy observations.

2.5. Microstructure characterization

The samples were examined in Back Scattered Electrons mode (BSE) using a JEOL JSM-6010LA Scanning Electrons Microscope (SEM) equipped with an Energy Dispersion Spectrometer (EDS). The general chemical composition was controlled in three randomly chosen × 250 zones. The chemical composition of the matrix was also subjected to three EDS measurements for the three states – as-cast, aged at 1400 K and aged at 1510 K – at × 1000 and with spot analyses. Spot EDS analyses were also carried out on the coarsest particles existing in the