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To cite this version:
Patrice Berthod. Avoiding or Promoting Graphite in Carbon-Rich Chromium-Containing CoNiFe Cast Alloys-Part 1: Preliminary Thermodynamic Exploration. ISRN Thermodynamics, International Scholarly Research Network, 2012, 10.5402/2012/308795 . hal-02334384

HAL Id: hal-02334384
https://hal.archives-ouvertes.fr/hal-02334384
Submitted on 26 Oct 2019

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Research Article

Avoiding or Promoting Graphite in Carbon-Rich Chromium-Containing CoNiFe Cast Alloys—Part 1: Preliminary Thermodynamic Exploration

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Received 2 February 2012; Accepted 2 March 2012

Academic Editors: A. Chagovetz and D. Chakrabarti

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The thermodynamic equilibria of alloys, based on Co, Ni, and Fe rich in chromium and carbon over a [500; 1500 °C] range of temperature, were determined using thermodynamic calculations. The probable types of microstructures (hypo- to hypereutectic) as well as the phase present at high temperature (matrix network, types of carbides, presence or not of graphite) were predicted. From these results new chromium contents to either avoid or promote the presence of graphite were chosen and the as-cast microstructures of the corresponding real alloys were anticipated, before their elaboration and microstructure characterization in this second part of this work.

1. Introduction

Alloys of cobalt, nickel or iron and containing chromium, and carbon in moderate quantities (typically lower than 1 wt.% C) are the bases of many superalloys [1] to which chromium brings the desired resistance against high-temperature oxidation and corrosion [2] and in which carbides ensure good mechanical resistance at all temperatures. Other materials, with similar global chemical compositions but containing much more carbon with the form of numerous carbides, exist for other applications requiring high hardness and wear resistance.

There are thus cobalt alloys for cutting tools [3] which are composed of a cobalt matrix containing high amounts of dispersed WC carbides, or for coatings [4] which consist in Co-W2C deposited by thermal spray on steels. In the same way carbon can be present in great quantities in {Ni, Cr}-based alloys in order to obtain high levels of hardness [4–6] and in bulk [7] or hardfacing coatings [8] for {Fe, Cr}-based alloys for the same purpose.

First studies were undertaken for 30 wt.% Cr-containing Co-based [9], Ni-based [10], and Fe-based [11] ternary alloys with carbon varying from 2.5 to 5 wt.% for exploring the microstructures of alloys of these families when they are elaborated by classical foundry. If very high values of carbides fractions, and consequently high hardness, were observed, it appeared that it is possible that graphite appears in the as-cast microstructures but at different carbon levels depending on the base element. In the present study it was undertaken to better know the circumstances of presence or of absence of the graphite phase, this time concerning the chromium content.

This was done by performing preliminary thermodynamic calculations to anticipate the possible effects of variations in chromium content on the phases which may exist for these three ternary systems. This is the subject of this first part of the work.

In the second part new alloys with lower chromium contents or with higher chromium contents for given carbon contents will be elaborated and characterized by metallography.

2. Model Description and Chosen Compositions for Calculations

2.1. Alloys Selected as Points of Departure for the Study

The initial high carbon 30 wt.% Cr-containing alloys which were
considered for the beginning of this work are (all contents in weight percents) the following:

(i) the three Co-based alloys Co-30Cr-3C (Co30), Co-30Cr-4C (Co40), and Co-30Cr-5C (Co50) [9],
(ii) the three Ni-based alloys Ni-30Cr-3C (Ni30), Ni-30Cr-4.5C (Ni45), and Ni-30Cr-5C (Ni50) [10],
(iii) and the three Fe-based alloys Fe-30Cr-3C (Fe30), Fe-30Cr-4C (Fe40), and Fe-30Cr-5C (Fe50) [11].

In these previous studies it was seen that the cobalt alloys were very rich in carbides, but it was also noted the appearance of another carbon-rich phase—graphite (100% C)—in the as-cast microstructures of the carbon-richest among them (for carbon contents of 4.5 and 5 wt.%). Graphite was also present, in higher quantities, in the as-cast nickel alloys containing between 4 and 5 wt.% C, but it never appeared in the iron alloys whatever the carbon content between 2.5 and 5 wt.% C.

2.2. Selection of New Versions of Alloys Using Thermodynamic Calculations. In the present study the possible high amounts of graphite which may be achieved were explored for some Co-based (Co30, Co40, and Co50) by lowering, in their chemical compositions, the content in the strongest carbide-forming element present: chromium. Second, for some of the Ni-based alloys containing graphite (Ni45 and Ni50), new chromium contents, higher than the initial 30 wt.% Cr, were tested to prevent the appearance of the too soft graphite (phase potentially detrimental for the hardness of the alloys). Third, for some of the initial graphite-free Ni-based (Ni30) and Fe-based alloys (Fe30 and Fe40), the limits of graphite appearance were explored by considering new chromium-lowered versions of these alloys. Finally, with a chromium-enriched version of the carbon-richest iron alloy (Fe50), it was examined if additional chromium in moderate quantity permits a detectable new increase in carbide fraction and therefore of hardness.

The preliminary calculations aimed to select new chromium contents for several carbon contents chosen for each ternary system. They were performed using the Thermo-Calc [12] software working with a database containing the descriptions of the Co-Cr-C, Ni-Cr-C, and Fe-Cr-C systems and their corresponding subsystems (resp., [13–18], [17, 19, 20],...
Figure 2: Isopleths at constant Cr content for the Ni-Cr-C system, showing the phases' evolution when the Cr content increases from 25.5 to 37 wt.% for the same [2.5; 5.5 wt.%] carbon content range; position of the initial alloys (doted lines) and of the Cr-modified alloys (solid lines).

3. Results and Discussion

3.1. Thermodynamic Calculations. Thermo-Calc calculations were additionally run to obtain sections at the selected different chromium contents: 30 wt.% Cr as reference for the three M-Cr-C systems and for three other Cr contents for each of them:

(i) Co-12Cr-3C (named “Co30/12Cr”), Co-15.5Cr-4C (named “Co40/16Cr”), and Co-23Cr-5C (named “Co50/23Cr”),
(ii) Ni-25.5Cr-3C (named “Ni30/26Cr”), Ni-34.5Cr-4.5C (named “Ni45/35Cr”), and Ni-37Cr-5C (named “Ni50/37Cr”),
(iii) and Fe-19.7Cr-3C (named “Fe30/20Cr”), Fe-26.1Cr-4C (named “Fe40/26Cr”), and Fe-32.6Cr-5C (named “Fe50/33Cr”).

in all cases for $x \in [2.5; 5.5]$ and all contents being expressed in wt.%. The calculated isopleths are presented in Figures 1, 2, and 3, respectively for the Co-$y$Cr-$x$C, Ni-$y$Cr-$x$C, and Fe-$y$Cr-$x$C systems. They are all calculated and drawn for the [2.5; 5.5 wt.% C] range of carbon contents, and for temperatures higher than 500°C, temperature at which it is reasonable to consider that the cooling rate is high enough to obstruct further solid state transformations notably concerning carbides and graphite. Each figure contains first the 30 wt. Cr-section of the ternary diagram which serves as reference. In this section the reference 30Cr-containing alloys are represented by dotted lines. The other diagrams are the sections of the same ternary diagram but for the other values of the chromium content. In each of these three other sections, the Cr-modified alloys studied here are represented by a solid line.

3.2. Cobalt Alloys. In the 30 wt.% Cr-section one find again that the graphite phase can be encountered for 4 wt.% C and more, while it cannot appear for lower carbon contents. It appears at the end of solidification, but it should disappear during the cooling under 800°C if the alloy contains less than about 4.5 wt.% C. For higher carbon contents, graphite should remain in the alloys at least until reaching 500°C.
Solidification should start with the crystallization of austenite (FCC cobalt matrix) for carbon contents up to about 3.5 wt.% C and, in contrast, with an early precipitation of carbides (more precisely M7C3) for higher carbon contents. One can remind that this absence or presence of graphite, as well as the hypoeutectic or hypereutectic character (presence of dendrites or presence of coarse primary carbides), was effectively noted in the Co30, Co40, and Co50 real alloys [9].

If the chromium content is lowered to 23 wt.%, the eutectic point is moved left, with also an extension of the graphite-containing domains towards lower carbon contents, with as result the possible existence of small quantities of graphite for the 3.5 wt.% C-containing alloy, and even for the one containing 3.0 wt.% C if the cooling rate does not allow the small quantity of graphite, appeared at solidification, disappearing. In addition graphite may appear as first solid phase to crystallize for the 5 wt.% C-containing alloy, which will be thereafter elaborated. A new impoverishment of chromium down to 16 wt.% Cr may lead to a eutectic graphite precipitation in all alloys whatever the carbon content in the considered range [2.5; 5.5 wt.% C]. The alloy with 4 wt.% C, which will be really elaborated, should display a eutectic microstructure. To finish, for a strongly lowered Cr content, 12 wt.% Cr, graphite should be very present, and proeutectic graphite should be encountered in alloys containing more than 3.7 wt.% C. In contrast, the 12 wt.% Cr alloy which will be really synthesized should be of a hypoeutectic type, with presence of dendrites but also of a great quantity of graphite.

The quantitative results of the thermodynamic calculations for 500°C are displayed in Table 1 for the total mass fractions of carbides (all types together) and for the mass fraction of graphite. One can see that graphite should be present in significant quantities in these Cr-impoverished versions of the initial 30Cr-containing alloys. Indeed up to 1.5-1.6 mass% of graphite may be obtained in the two carbon-richest alloys. In contrast the expected carbide fractions would be severely decreased, following this new “use” of a part of the carbon contained in the alloys.

### Table 1: Thermodynamic calculations for the Co-based alloys (mass fractions at the equilibrium at 500°C).

| Co-xCr-3C | Co-30Cr-4C | Co-30Cr-5C |
|-----------|------------|------------|
| wt.%      |            |            |
| 30        | 12         | 30         | 15.5       | 30         | 23         |
| Carbides  | 34.6       | 13.82      | 36.85      | 17.88      | 34.6       | 26.52      |
| Graphite  | 0          | 1.15       | 0          | 1.61       | 0.38       | 1.46       |

3.3. Nickel Alloys. For the Ni-Cr-C system, one can see in the 30 wt.% Cr-section, for a carbon content varying from...
2.5 to 5 wt.%, that all the alloys would be hypereutectic since the first crystal to precipitate at the beginning of solidification is either a carbide (M7C3 for the C-lowest side, M3C2 for higher C contents) or graphite (for the C-highest side). In the second case the graphite appearance is followed by the crystallization of M3C2 carbide before the metallic FCC matrix appears, phases which were effectively observed in the as-cast real alloys at room temperature [10]. This is also true for the three other sections presented (for 25.5, 34.5, and 37 wt.% Cr and the same range of C content).

When the chromium content increases from 25.5 to 37 wt.%, there is a general movement of all the domains in the right direction, with as first consequence a decrease of the width of the carbide-containing domains. In contrast, this also induces the appearance of the {FCC matrix-M3C2-M7C3} domain, then of the {FCC-M7C3} one for higher Cr content, followed by the rightward shift of these two domains. At the same time the widths of the {FCC matrix-M3C2} and {FCC matrix-M3C2-M7C3} domains remain constant, while the width of the {FCC matrix-M7C3} domain increases.

If one finds again, in the 30 wt.% Cr-section, that the Ni30 alloy should be free of graphite and that the Ni45 and Ni50 would contain graphite, the three new alloys, represented by solid lines in the 25.5 wt. Cr, 34.5 wt.% Cr, and 37 wt.% Cr-sections, are all just on the left of the boundaries delimiting the graphite-containing domains on the right, over the whole considered temperature range. Thus, these three new alloys, which will be elaborated, would be graphite-free, as targeted by the choice of the new contents of the carbide-former element.

Table 2 displays the values of the mass fractions of carbides (M3C2, M7C3, or the sum of the two) and of graphite, for the equilibrium states at 500°C. One can see that the increase in chromium content should effectively avoid graphite for the Ni45 and Ni50 alloys, simultaneously with a significant increase in carbide fraction (up to more than 37 mass % for the C-richest alloy). In contrast the decrease of the Ni30 chromium content down to 25.5 induces a decrease in carbide fraction (about 3-4 mass %), but it does not promote the appearance of graphite.

3.4. Iron Alloys. Finally, concerning the Fe-Cr-C system, one can see that the 30 wt.% Cr section is, for the [2.5; 5.5 wt.% C] × [500; 1500°C] area, mainly constituted by a {matrix + M23C6 carbides} domain, matrix being FCC above an almost horizontal line at about 800°C, and BCC bellow. A vertical band delimited on the right by 3 wt.% C corresponds to the same matrixes at the same temperatures but mixed with both M23C6 and the carbon-lower M23C6 carbides. The carbon range corresponds essentially to hypereutectic composition since the eutectic carbon content is about 3 wt.%. The three iron alloys selected to be the points of departure of chromium change would be almost eutectic (Fe30) or hypereutectic (Fe40 and Fe50). Furthermore, they would be graphite-free for Fe30, Fe40, and even Fe50 since the possible appearance of graphite in this alloy bellow about 600°C is not reasonably expected since this supposes nucleation and growth of graphite by solid-state transformation at such low temperature and for too short time (cooling). Two types of carbides may exist since M7C3 is the stable form over a wide range of high temperatures, but M3C2 may potentially appear in Fe50 and possibly in Fe40, near 500°C. However, because of the rather fast cooling again, it can be thought that M23C6 should be the single (or at least the main) carbide still present at room temperature. The absence of graphite and the existence of M23C6 as single carbide were effectively observed in the as-cast Fe30, Fe40, and Fe50 alloys [11].

When the chromium content is decreased to almost 26 wt.% and, after, down to almost 20 wt.% there is a general movement towards the left, with consequently the disappearance of the two carbides-containing {FCC or BCC + M23C6 + M7C3} domain, and the appearance, then progress towards lower carbon contents, of a cementite-containing domain as well as the development of the graphite-containing one. Thus, there is, for alloys with carbon contents varying in the same range as the alloys previously studied [11], a significant risk of appearance of graphite and cementite. However, for reasons of more or less high easiness of nucleation and growth by solid-state transformation at such low temperatures, cementite may be more likely expected than graphite.

The new alloys, for which the chromium (and carbon) contents were especially chosen to avoid the precipitation of such phases above 500°C, would be both cementite-free and graphite-free. For them, as for the new cobalt-based and nickel-based alloys above, calculations were performed for 500°C to assess the theoretic mass fractions at this temperature (Table 3). But additional calculations were also
performed at 600°C (Table 4) to take into account the fact that the “microstructure-freezing temperature” is of course not so precise and the as-cast microstructures which will be obtained may correspond (approximately) to the stable state calculated at 500°C as well as to a one calculated for temperatures 100 or 200°C higher. This was important to do that for iron alloys since the carbide fraction may abruptly vary just before 500°C because of the appearance of the C-rich M₇C₃ carbides. Indeed, according to Thermo-Calc, if the carbides are M₇C₃ at 600°C in the Fe30/20Cr, Fe40/26Cr, and Fe50/33Cr, they are totally replaced with M₇C₃ at 500°C in these alloys. One can note that it is also the case of the initial Fe50 alloy. Consequently the carbides mass fractions are significantly higher at 600°C than at 500°C for all the three new alloys. Finally one can remark that the M₇C₃ carbide fractions of the Fe30 and Fe40 are a little higher at 600°C than at 500°C although the contrary can be expected. This is due to the fact that Cr and Fe are together involved in the compositions of these carbides (this is also true for Ni and Co which coexist in the M₇C₃ carbides present in some Co-based and Ni-based alloys resp.), in contrast with the M₇C₃ carbides which only contain Cr. And the composition of the most stable carbides varies with temperature when they are M₇C₃. The same reason explains the small increase in M₇C₃ carbides when the Cr content decreases (the original and modified Fe30 and Fe40 alloys at 600°C) and their small decrease when the Cr content increases from the original Fe50 to the modified Fe50 alloy. The following example allows illustrating that the original Fe40 should contain 54.80 mass % of BCC matrix (Fe-0.71Cr-0.00073C in wt.%) and 45.20 mass% of M₇C₃ (65.51Cr-25.64Fe-8.85C in wt.%) while the Fe40/26Cr should contain 54.53 mass% of BCC matrix (Fe-0.44Cr-0.00144C in wt.%) and 45.47 mass% of M₇C₃ (56.87Cr-34.33Fe-8.79C in wt.%).

4. Conclusion
Thermodynamic calculations were here of a good help for anticipating the microstructure changes resulting from the modification of the chromium content in these nine ternary carbon-rich alloys belonging to three different families: Co-based, Ni-based, and Fe-based alloys. One can expect that these predictions and the resulting choices of Cr content for the new alloys, wished to contain graphite or not, will be in conformity with reality although that the as-cast microstructures which will be obtained surely will not respect the conditions of thermodynamic equilibrium at all the temperatures which will be known by the alloys during their solidification and postsolidification cooling. In the second part of this work, these new alloys will be really elaborated, and their as-cast microstructures will be characterized and compared to the results of thermodynamic calculations.

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