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Influence of the chromium content on the as-cast microstructures of ternary alloys very rich in carbon: Part II: Ni-based and Fe-based alloys with 3 to 5 wt.%C

Patrice Berthod[1, 2*], Elise Souaillat[1], Ophélie Hestin[1], Thierry Schweitzer[2]

[1]University of Lorraine, F.S.T., B.P. 70239, 54506 Vandoeuvre-les-Nancy, (FRANCE)

[2]Institut Jean Lamour (UMR 7198), Team 206 "Surface and Interface, Chemical Reactivity of Materials" B.P. 70239, 54506 Vandoeuvre-les-Nancy, (FRANCE)

E-mail : Patrice.Berthod@ijl.nancy-universite.fr

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ABSTRACT

High fractions of carbides are favourable for high hardness but the possible presence of graphite for very high carbon contents may have the opposite effect. Limited modifications of the chemical composition may correct the microstructures to achieve the demanded properties. This was studied for three ternary alloys based on nickel and three other ones based on iron, all rich in carbon, by modifying their chromium contents (from 30wt.% Cr to new values comprised between 20 and 37wt.%). Preliminary thermodynamic calculations were first performed to explore the possible microstructures, and to select several chromium contents potentially allowing either to promote graphite, or on the contrary to avoid it, or to enhance the carbide fraction at constant carbon content. Second, alloys with the chromium contents selected above were really elaborated by foundry. Metallography samples were prepared and the as-cast microstructures observed. As in the first part of this work concerning cobalt alloys, the calculated and metallography results were compared to the ones previously obtained for the analogous nickel and iron containing 30wt.%Cr. Adding 4.5 and 7% of chromium to the graphite-rich nickel alloys Ni-30Cr-4.5C and Ni-30Cr-5.0C respectively, induces a significant decrease in graphite fraction while subtracting 4.5 %Cr to the graphite-free Ni-30Cr-3.0C is not sufficient to make graphite appear but it decreases the carbide's quantity. Removing 10.3% Cr and 3.9%Cr to the Fe-30Cr-4.0C ant the Fe-30Cr-5.0C respectively, decreases the mass fraction of carbides but does not promote the appearance of graphite. In contrast adding 2.6%Cr to the Fe-3Cr-5.0C induces only a small increase in carbide quantity.

KEYWORDS

Nickel alloys;
Iron alloys;
High chromium;
Very high carbon;
Thermodynamic calculations;
Carbides;
Graphite.

INTRODUCTION

The alloys based on nickel and/or iron and containing high amounts in chromium, an element which is especially useful to resist high temperature oxidation[1], represent important families of superalloys[2]. When carbon is also present in high quantities, nickel-based alloys[3-6] (and iron-based alloys[7, 8]) are able to display high hardness thanks to the presence of large fractions of chromium carbides and to the very high values of hardness of these carbides[9]: $Cr_{23}C_6$ (1650 Hv_{50g}), Cr_7C_3 (1336 Hv_{50g}) or Cr_3C_2 (1350 Hv_{50g}). Such alloys used as bulk alloys or as hard-facing coatings may be involved in friction applications for which a good wear-resistance is required.

The simultaneous presence of carbon and chromium in high contents is favourable for obtaining high volume fractions of carbides with consequently high values of hardness for the alloys. However it is also possible in some cases that this leads to the appearance of the soft phase graphite which is in contrast detrimental for this property. As the cobalt alloys studied in the first part of this work[10], nickel alloys are particularly concerned since it was already observed that, even for chromium as high as 30wt.%, lamellar graphite may appear when the carbon content is very high (between 4 and 5wt.%C)[11]. One can think that the addition of more chromium may lead to a decrease in graphite fraction – and even its disappearance - for a given carbon content. Such Cr addition appears to be, by this way, favourable to the hardness of the alloy. Inversely some of the graphite-free alloys may contain too high quantities of the expensive chromium element and one can think that their chromium contents may be interestingly a little decreased without appearance of graphite. This is the case of the carbon-lowest nickel alloys previously considered[11] and of all the iron alloys also earlier studied[12].

The purpose of this second and last part is to study the effect on the graphite presence, as well as on the carbide's fractions, of variations in chromium content in the case of nickel-based and iron-based alloys selected among the 30wt.%Cr-containing high-carbon alloys previously studied.

EXPERIMENTAL

Alloys of interest

Three nickel-based alloys, Ni-25.5Cr-3C ("Ni30 with 25.5wt.%Cr"), Ni-34.5Cr-4.5C ("Ni45 with 34.5 wt.%Cr") and Ni-37Cr-5C ("Ni50 with 37 wt.%Cr"), and three iron-based alloys, Fe-19.7Cr-3C ("Fe30 with 19.7 wt.%Cr"), Fe-26.1Cr-4C ("Fe40 with 26.1 wt.%Cr") and Fe-32.6Cr-5C ("Fe50 with 32.6wt.%Cr") were considered. Accordingly to above, the "Ni45 with 34.5wt.%Cr" and "Ni50 with 37wt.%Cr" alloys were considered in order to see if such increases in chromium are high enough to avoid graphite in these two alloys which were especially rich in this phase for 30wt.%Cr, while the "Ni30 with 25.5wt.%Cr", the "Fe30 with 19.7wt.%Cr" and "Fe40 with 26.1wt.%Cr" alloys were considered to see if the chromium contents in the 30wt.%Cr-containing corresponding alloys can be decreased by keeping their graphite-free character in order to be less costly. The objective of the "Fe50 with 32.6wt.%Cr" alloy was other: seeing if the carbide fraction can be increased another time by adding more chromium, but in a limited manner to do not risk the precipitation of brittle phases rich in chromium.

Initial thermodynamic calculations

Thermodynamic calculations were performed before any alloy's synthesis to anticipate the microstructures which may appear. For that, the N-version of the Thermo-Calc software[13] was used with a database containing the descriptions of the ternary systems Ni-Cr-C and Fe-Cr-C and their sub-systems[14-22]. The theoretic stable microstructures were determined for the temperatures spread over the 1500°C $\rightarrow$ 0°C interval. However the lowest part, from about 500°C down to 0°C, is not representative of reality for kinetic reasons and it is why the right side of the graphs of phase's evolution versus temperature will be thereafter shaded in red for the Ni alloys or in purple for the Fe alloys.

Elaboration and metallographic characterization of the alloys

The six alloys were elaborated by fusion-solidification in a CELES high frequency induction furnace under inert atmosphere (argon). In each case the pure elements (pure nickel or iron, and chromium: Alfa Aesar, > 99.9 wt.%; carbon: graphite) were melted in the copper crucible (cooled by intern water circulation) of the furnace under 300mbars of pure Ar. This led to ingots of about 40g, which were thereafter cut to be embedded in a ESCIL cold resin mixture then polished with SiC papers from 240 to 1200 grit. A mirror state was achieved by final polishing using a textile disk enriched in 1µm alumina particles.

A Scanning Electron Microscope (SEM: Philips, model XL30) was used for the microstructure observations, which were done essentially in the Back Scattered Electrons mode (BSE) under an acceleration voltage of 20kV. Electronic micrographs were taken at ×500, to illustrate the microstructures.

RESULTS AND DISCUSSION

Nickel-based alloys

Ni45 with 34.5 wt.%Cr by comparison to the initial Ni45 with 30wt.%Cr[11]

The theoretic sequences of solidification and of cooling in the solid state of both alloys are described in Figure 1. According to Thermo-Calc the Ni45 with 34.5Cr ought to start solidifying between 1500 and 1400°C, as the initial Ni45 alloy. Before completed solidification two types of carbides are present, M_3C_2 (more precisely Cr_3C_2) and the M-richer M_7C_3 (M = Cr and Ni simultaneously, about 74Cr and 18Ni in wt.%), in contrast with only M_3C_2 for the initial Ni45. The M_7C_3 carbides disappear before reaching 1200°C and the M_3C_2 are the single type of carbides present, as for the initial Ni45. In the new alloy M_7C_3 would appear again between 400 and 300°C, but probably very moderately (very low transformation kinetics at such low temperatures. Another main difference is the absence of any graphite in the Cr-enriched alloy, while this soft phase appeared at solidification in the initial Ni45 (with mass fraction up to 0.7%) and remained thereafter. The total carbide fraction (M_3C_2+M_7C_3) varies from 31 to 39 mass.% in the Ni45 with 34.5Cr against 25 to 34 mass.% in the initial Ni45. Thanks to the higher chromium content the total carbon is thus involved in carbides (but a part is also in solid solution in the matrix).

The real alloy which was obtained by foundry practice displays a hyper-eutectic microstructure composed of coarse pro-eutectic carbides and a {carbide + matrix} – eutectic, as the initial Ni45 alloy (Figure 2). However graphite has not totally disappeared with the Cr-enrichment since rare particles are still present. The supplementary quantity of chromium was obviously not high enough to totally avoid the precipitation of graphite. This mismatch between calculations and real elaboration is possibly to attribute to the real solidification and solid state cooling which were not slow enough for allowing a good respect of the equilibrium conditions.

Ni50 with 37 wt.%Cr by comparison to the initial Ni50 with 30wt.%Cr[11]

The enrichment in chromium of the graphite-rich initial Ni50 alloy was chosen to be as high as 37wt.%. Such modification should involve an increasing in liquidus temperature up to a higher value (Figure 3) but the latter was still compatible with a total fusion with the furnace used. More chromium should lead to a too high melting temperature which may be not achieved in reality. Nevertheless this high chromium content should lead, according to Thermo-Calc, to a solidification starting higher than 1500°C. The first phase to appear is the M_3C_2 (Cr_3C_2) carbide, the mass fraction of which reaches about 16 mass.% before a second solid phase appears (M_7C_3 with an additional fraction of about 10% in mass). With this chromium content graphite is not totally avoided: it should appear at the end of solidification near 1200°C with a quantity of about 1.2 mass.% but disappear just after, against the same quantity of 1.2 mass.% at high temperature but remaining until room temperature with about 0.4 mass.% for the initial Ni50 alloy. As already seen for the Cr-modified alloy, the M_7C_3 carbides would disappear at high temperature during the solid state cooling, but appear again at low temperature. The expected total mass fraction of carbides may increase from 35 to 42% in mass fraction, against 25.5 to 34.5 mass.% in the initial Ni50 alloy.

Thus the applied increase in chromium may lead to both a significant decrease of the graphite quantity and an increase in carbide fraction. The first difference is obvious between the microstructure obtained for the new alloy and the initial one (Figure 4), even if the graphite quantity seems to be little higher than in the previous Cr-enriched Ni45 alloy. In contrast, the quantity of carbides does not seem to be significantly higher than the one of the initial Ni50 alloy.

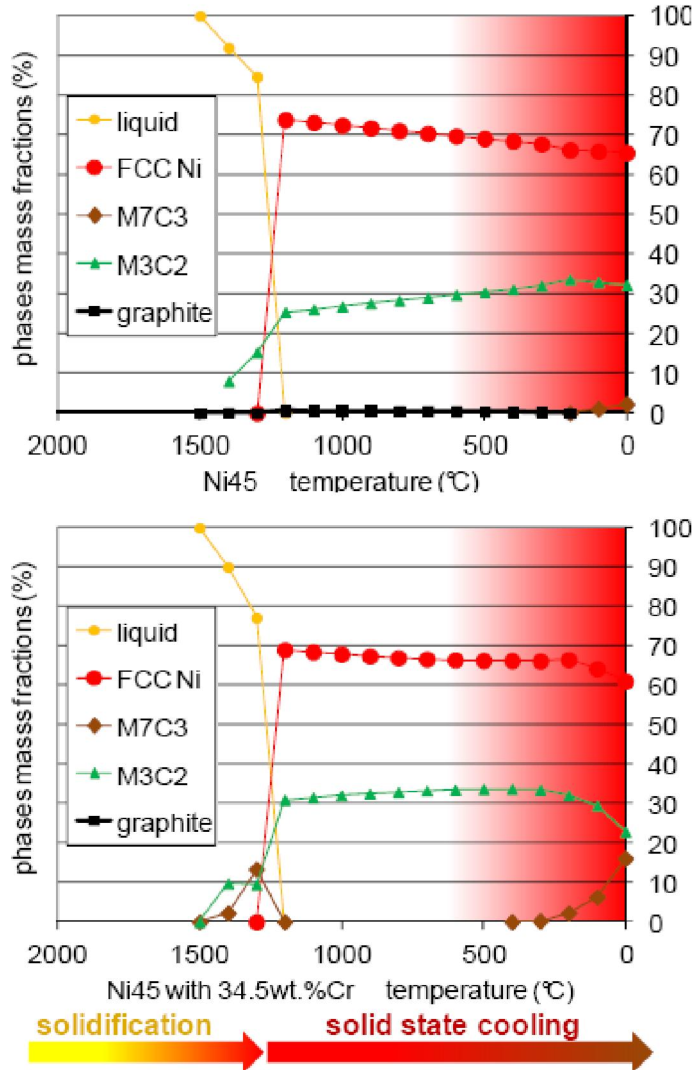

Figure 1 : The stable metallurgical states, versus temperature, of the two "Ni45" alloys: the earlier studied one [11] with 30wt.%Cr (top) and the new one with 34.5wt.%Cr (bottom), as calculated by Thermo-Calc; qualitative illustration of the microstructures development during the solidification progress

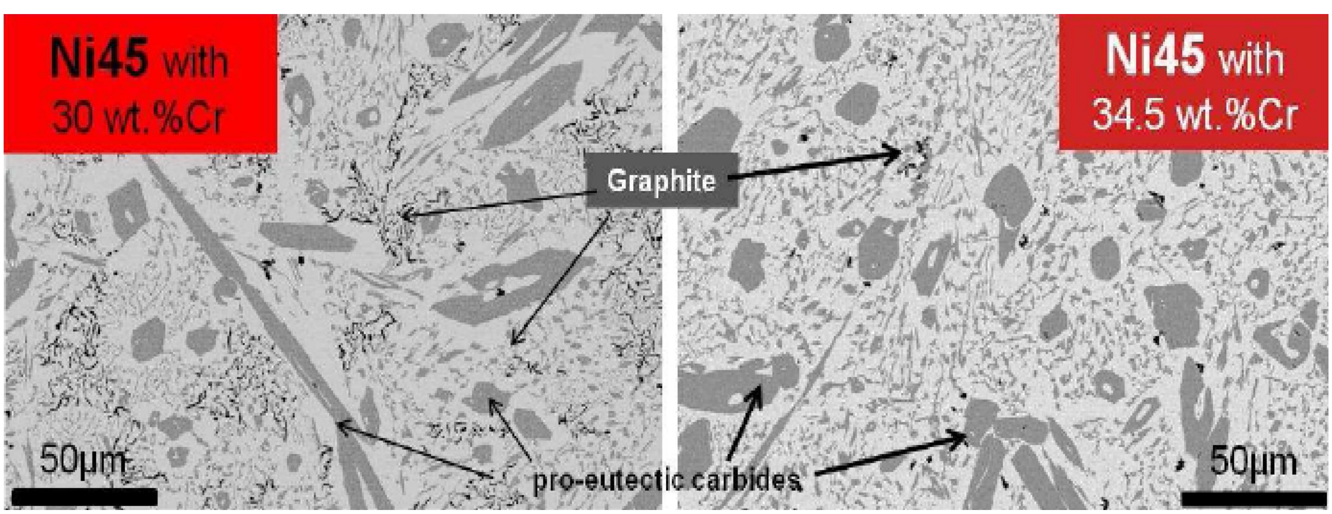

Figure 2 : Microstructures of the alloys Ni45-30Cr (left) [11] and Ni45-34.5Cr (right) in their as-cast conditions; SEM/BSE micrographs (magnification: x500)

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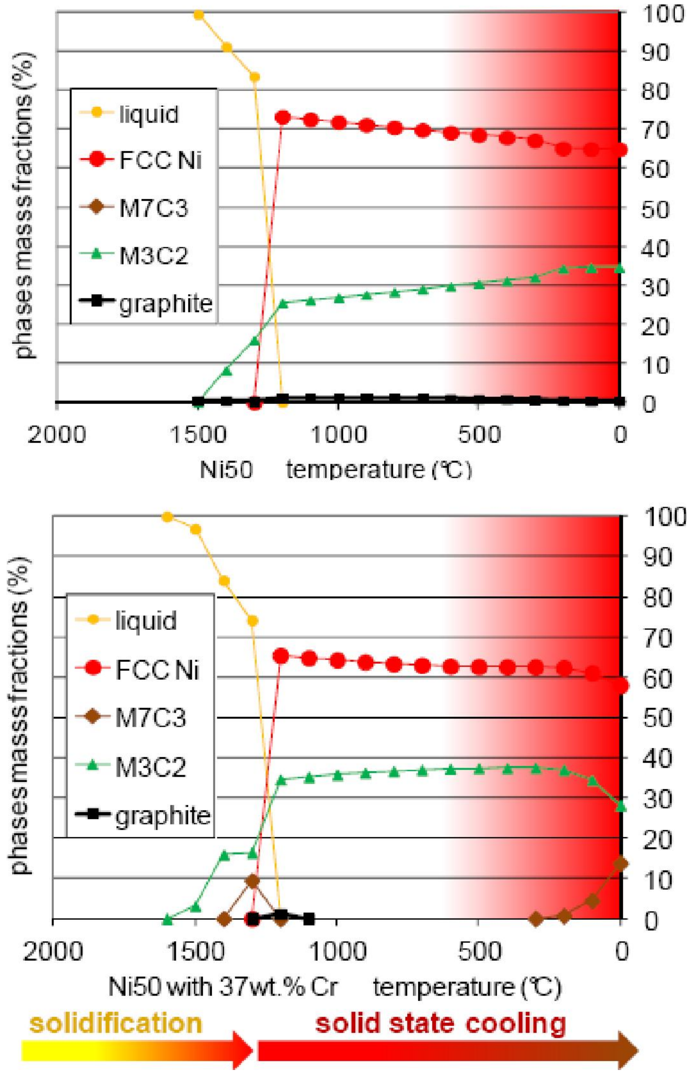

Figure 3 : The stable metallurgical states, versus temperature, of the two "Ni50" alloys: the earlier studied one [11] with 30wt.%Cr (top) and the new one with 37wt.%Cr (bottom), as calculated by Thermo-Calc; qualitative illustration of the microstructures development during the solidification progress

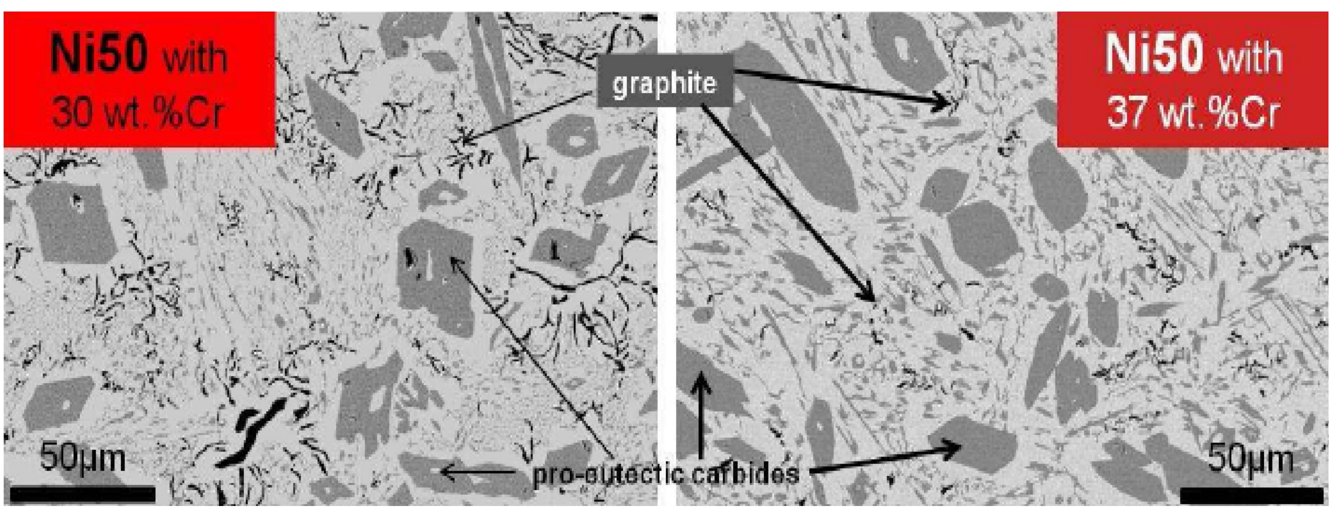

Figure 4 : Microstructures of the alloys Ni50-30Cr (left) [11] and Ni50-37Cr (right) in their as-cast conditions; SEM/BSE micrographs (magnification: x500)

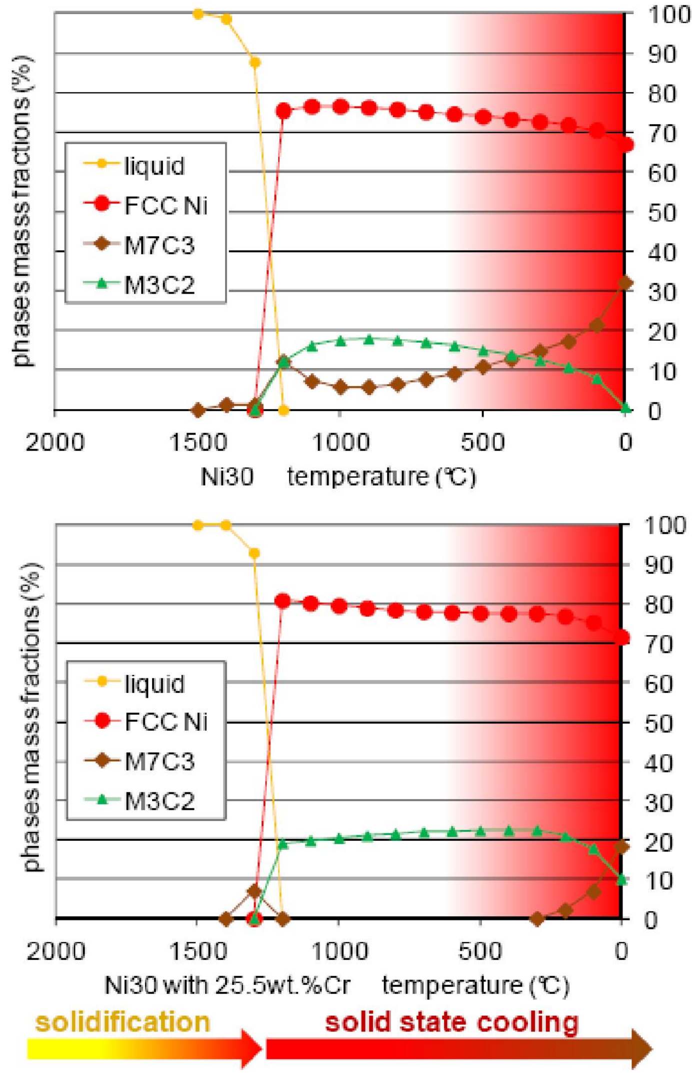

Figure 5 : The stable metallurgical states, versus temperature, of the two "Ni30" alloys: the earlier studied one [11] with 30wt.%Cr (top) and the new one with 25.5wt.%Cr (bottom), as calculated by Thermo-Calc; qualitative illustration of the microstructures development during the solidification progress

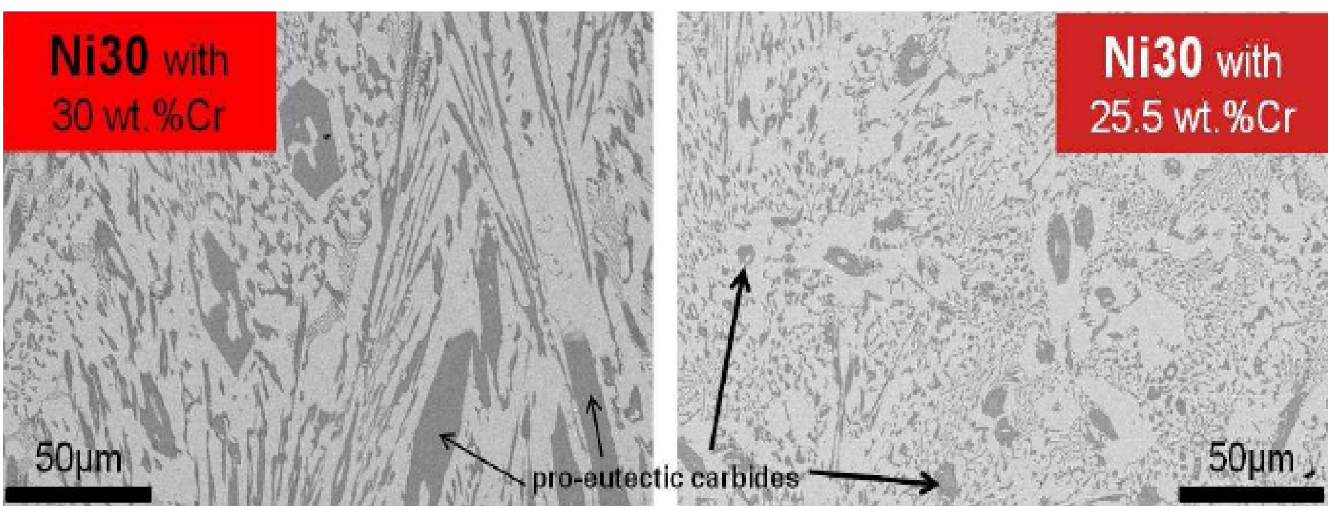

Figure 6 : Microstructures of the alloys Ni30-30Cr (left) 11 and Ni30-25.5Cr (right) in their as-cast conditions; SEM/BSE micrographs (magnification: x500)

Ni30 with 25.5 wt.%Cr by comparison to the initial Ni30 with 30wt.%Cr[11]

The objective of the modification of the chromium content in the Ni30 alloy was different: seeing if the Cr content can be lowered without appearance of graphite in this alloy which did not contained this soft phase. The preliminary thermodynamic calculations (Figure 5) showed that the chromium content can be lowered down to 25.5wt.% without graphite appearance, with in addition an only limited decrease in carbide fraction: from the {24 (high temperature) - 33 (room temperature) mass.% of M_7C_3 + M_3C_2} interval to the {19 (h. t.) - 29 (r. t.) mass.% of essentially M_3C_2 over the main part of the temperature interval} one.

This chromium decrease did not effectively lead to the presence of graphite in the real alloy but the decrease in carbide fraction seems being more significant than predicted (Figure 6). In addition the microstructure type, which was clearly hyper-eutectic in the initial Ni30 alloy (despite its moderate carbon content), has become only slightly hyper-eutectic.

Iron-based alloys

Fe30 with 19.7 wt.%Cr by comparison to the initial Fe30 with 30wt.%Cr[12]

The decrease of the chromium weight content of the Fe30 alloy from the initial 30% value down to 19.7wt.% should preserve the graphite-free character of the alloy (Figure 7). Two consequences are expected: an increase in liquidus temperature (comprised between 1500 and 1400°C against between 1300 and 1200°C for the 30wt.%Cr-containing alloy) and a decrease in carbide fraction (near 25-30 mass.% of M_7C_3 at high temperature and near 22 mass.% of M_3C_2 at low temperature, against between 28 (h.t.) and 34 (l.t.) mass.% of almost only M_7C_3 for the same initial Fe30 alloy). Additionally the allotropic transformation of matrix (FCC $\rightarrow$ BCC) should occur at lower temperature (between 800 and 700°C, against between 900 and 800°C for the initial Fe30), accordingly to a less ferritizing effect of the chemical composition less rich in chromium.

When one examines the microstructures really obtained (Figure 8) it appears that effectively graphite did not appear, but also that the slight hyper-eutectic character is replaced by a character clearly hypo-eutectic (presence of dendrites of matrix).

Fe40 with 26.1 wt.%Cr by comparison to the initial Fe40 with 30wt.%Cr[12]

The decrease from 30 wt.% to 26.1 wt.% of chromium leads to similar changes for the microstructure of the Fe40 alloy concerning the existence of graphite and the natures and mass fractions of carbides: graphite still absent, total change of the high temperature M_7C_3 carbides into the low temperature M_3C_2 between 600 and 500°C, and total carbide fraction lowered to 45 (h.t.) - 30 (l.t.) mass.% against the 45 (h.t.) - 34 (l.t.) mass.% (Figure 9).

The real microstructure, still of the hyper-eutectic type, tends to be closer to the eutectic type than the one of the initial Fe40 alloy (Figure 10): less pro-eutectic carbides and more {carbide – matrix} eutectic compound.

Fe50 with 32.6 wt.%Cr by comparison to the initial Fe50 with 30wt.%Cr[12]

Increasing the chromium content with 2.6wt.% Cr more may not revolutionize qualitatively the Fe50 microstructure (Figure 11). One can only note a slight increase in carbide mass fraction, from 51 - 57% of M_7C_3 (high temperature) and 37.5 – 37.2% of M_3C_2 (low temperature) against 50 – 57% M_7C_3 (h.t.) and about 35% of M_3C_2 for the initial Fe50 alloy.

No evident difference can be noted between the real alloys (Figure 12).

General commentaries

After having successfully favoured the appearance of graphite in hard high-carbon cobalt-based alloys[10] by lowering the chromium content, it was here in contrast attempted to decrease the fraction of this phase in nickel alloys by increasing their chromium content to potentially improve their hardness. These tests, guided by preliminary thermodynamic calculations, effectively led to the disappearance of graphite, or at least significant decrease of its fraction in the microstructure. It can be noted that this was achieved also by keeping the hypereutectic character of the alloys.

The other tests were the exploration of the microstructures of the lower chromium versions of the graphite-free Ni30, Fe30 and Fe45 alloys. Despite the significant decrease in the content of the main carbide-

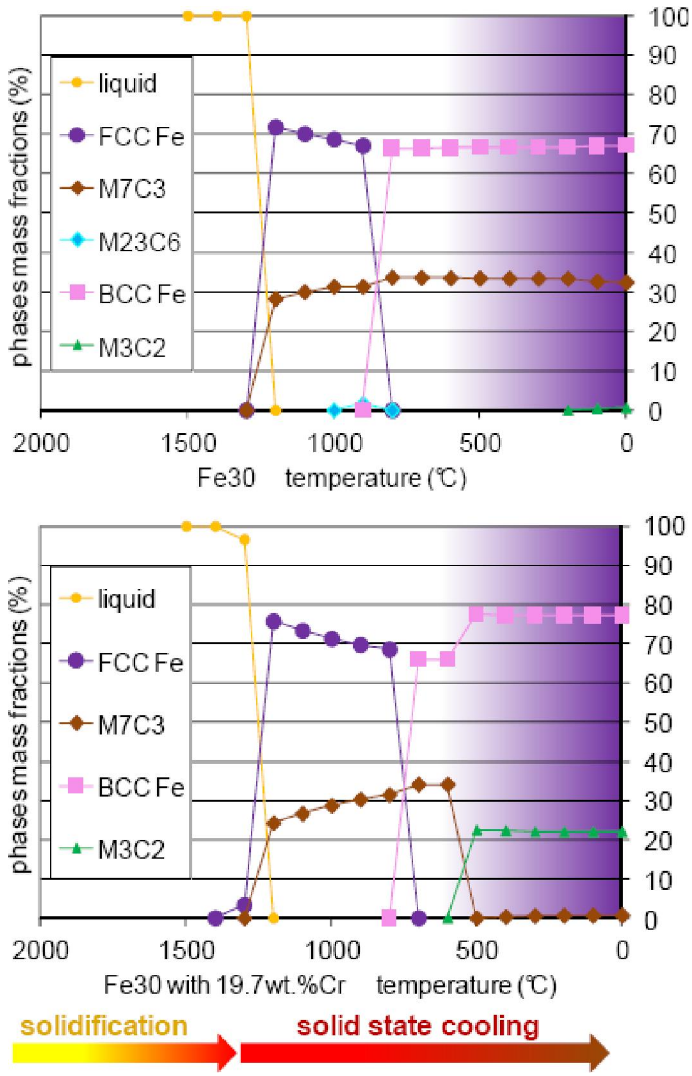

Figure 7 : The stable metallurgical states, versus temperature, of the two "Fe30" alloys: the earlier studied one [12] with 30wt.%Cr (top) and the new one with 19.7wt.%Cr (bottom), as calculated by Thermo-Calc; qualitative illustration of the microstructures development during the solidification progress

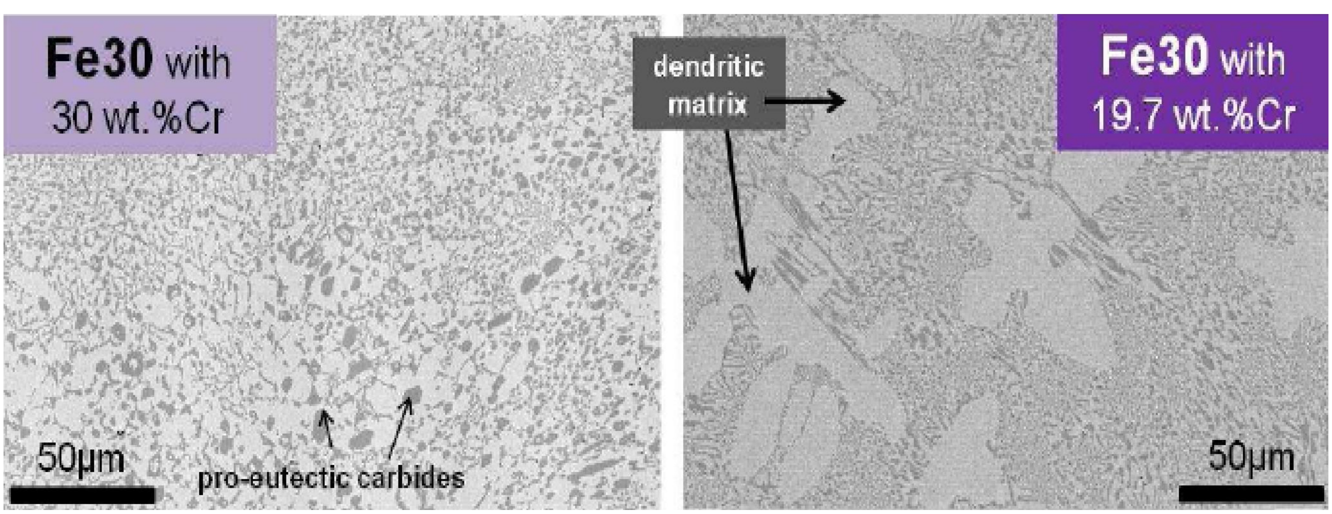

Figure 8 : Microstructures of the alloys Fe30-30Cr (left) 11 and Fe30-19.7Cr (right) in their as-cast conditions; SEM/BSE micrographs (magnification: x500)

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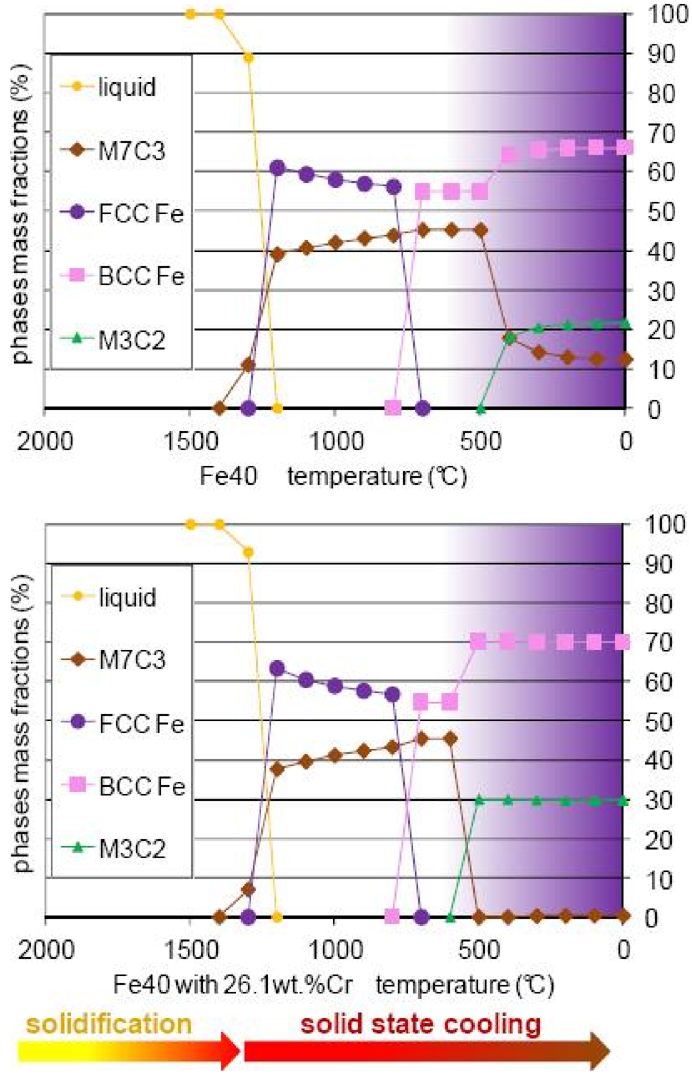

Figure 9: The stable metallurgical states, versus temperature, of the two "Fe40" alloys: the earlier studied one [12] with 30wt.%Cr (top) and the new one with 26.1wt.%Cr (bottom), as calculated by Thermo-Calc; qualitative illustration of the microstructures development during the solidification progress

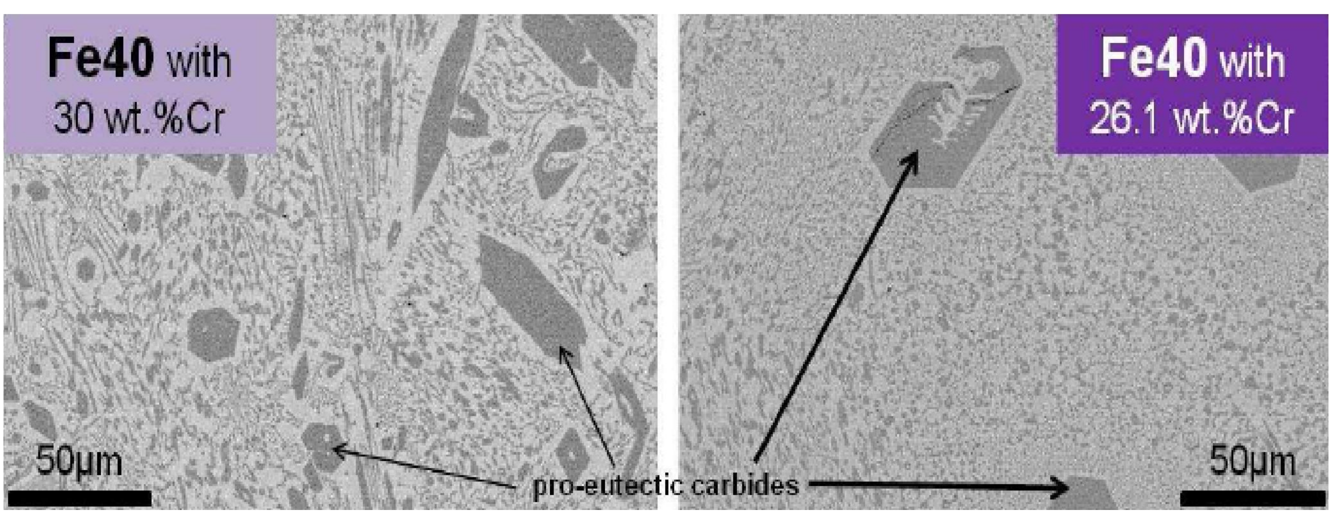

Figure 10 : Microstructures of the alloys Fe40-30Cr (left) 11 and Fe40-26.1Cr (right) in their as-cast conditions; SEM/BSE micrographs (magnification: x500)

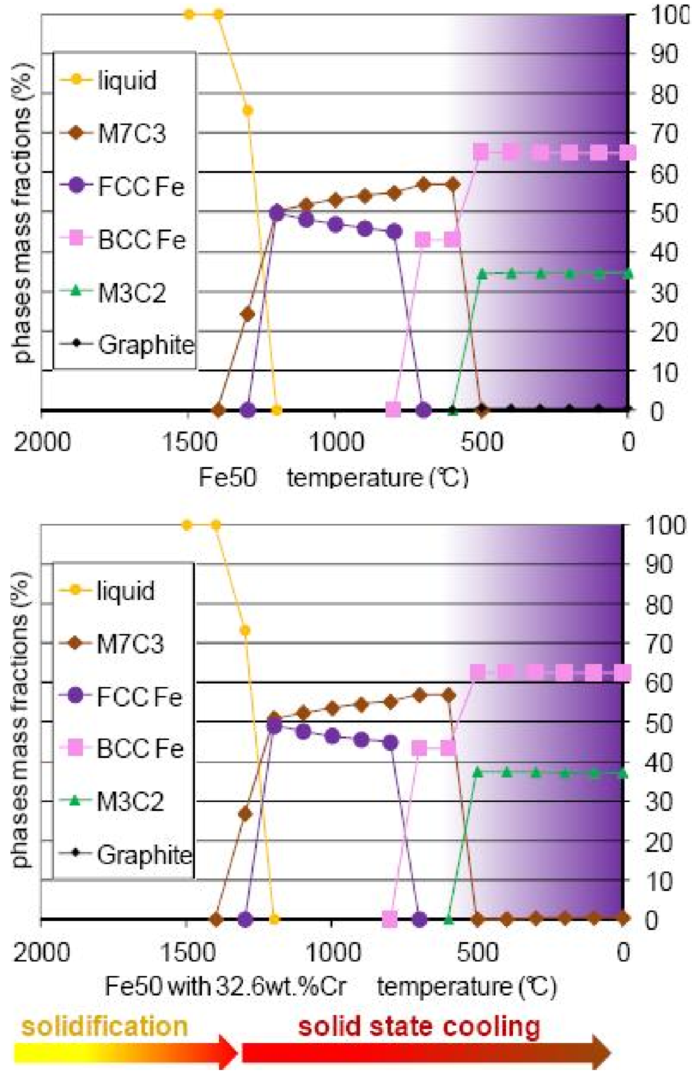

Figure 11 : The stable metallurgical states, versus temperature, of the two "Fe50" alloys: the earlier studied one [12] with 30wt.%Cr (top) and the new one with 32.6wt.%Cr (bottom), as calculated by Thermo-Calc; qualitative illustration of the microstructures development during the solidification progress

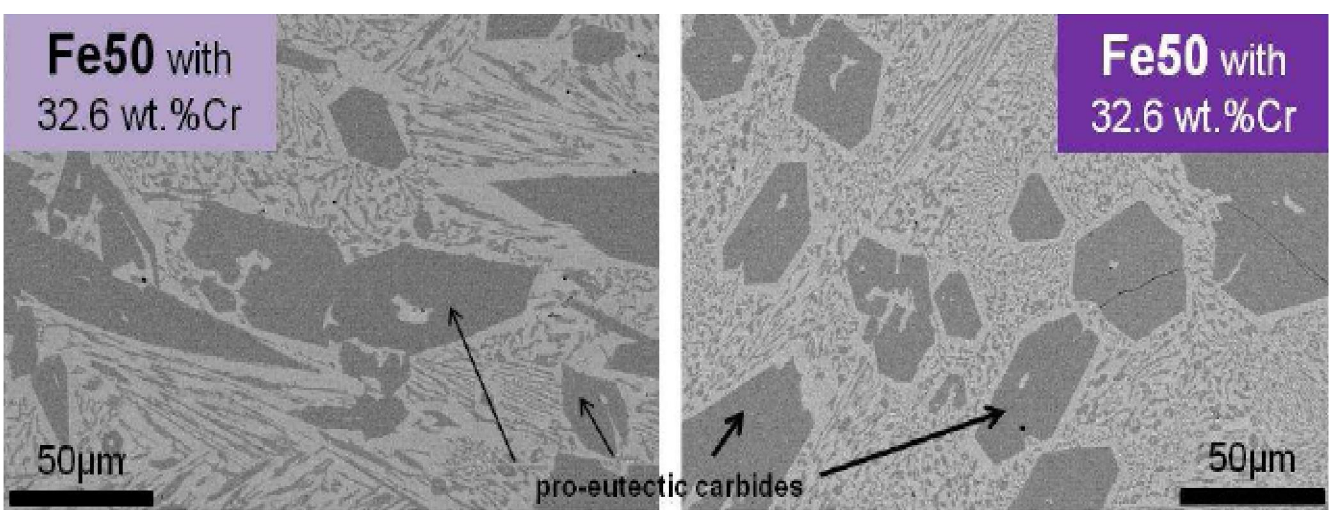

Figure 12 : Microstructures of the alloys Fe50-30Cr (left) 11 and Fe40-32.6Cr (right) in their as-cast conditions; SEM/BSE micrographs (magnification: x500)

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forming element the limits of graphite appearance were not reached. This allows obtaining less expensive Ni-Cr-C and Fe-Cr-C alloys containing less chromium and keeping potentially a high hardness thanks to the very high carbon contents in these alloys. Inversely it appeared also true that enriching in chromium a 5wt.%C-containing iron alloy did not really increase its carbide fraction in significant proportion.

CONCLUSIONS

In this last work concluding a general study concerning ternary alloys based on Cobalt, Nickel and Iron and rich both in chromium and carbon, it appeared that, farer than the important effect of carbon on the microstructures of 30wt.%Cr-containing alloys (type and fraction of carbides, hypo-, eutectic or hyper-eutectic characters, additional presence of graphite for very high contents), the chromium content may play also a noticeable role on the same characteristics. Such systematic study about alloys, which are elsewhere rather well known types of alloys for some of them, may show that the combination of carbon content and of chromium content possibly proposes many sets of hardness, high temperature corrosion resistance, thermal conductivity, and cost, all for a given mode of elaboration.

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