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Test of elaboration protocols for obtaining highly Co- or Ni -alloyed spheroidal cast irons from an industrial SG cast iron.Part A: first protocol. subpart 1: obtained microstructures

Kamel Meridja, Patrice Berthod*, Elodie Conrath

Institut Jean Lamour (UMR 7198), Team 206 "Surface and Interface, Chemical Reactivity of Materials" Faculty of Sciences and Technologies, University of Lorraine, B.P. 70239, 54506 Vandoeuvre-lès-Nancy, (FRANCE)

E-mail: Patrice.Berthod@univ-lorraine.fr

ABSTRACT

The fabrication of spheroidal graphite cast irons (SG iron), also known as ductile iron, is rather complicated since it involves a series of liquid iron treatments difficult to do. For obtaining a laboratory special SG cast iron with particular chemical composition, a possible way of elaboration can be re-melting of an industrial SG cast iron together with additional the element(s) to incorporate. This was earlier successfully realized in the case of silicon. In this work these are cobalt and nickel (and also iron for comparison) which were wished to be added in equal content as iron, with additionally silicon and graphite with quantities calculated to do not modify the final chemical composition. Unfortunately, here, the difficulty of incorporation of graphite led to increase both temperature and duration, with as result the loss of the spheroidal shape. Graphite was not nodular but its morphology as double in each alloy and varied with the nature of the added element. The metallic matrix was also dependent on the added element: ferrite-pearlitic, back centred cubic or austenitic. The responses to Nital etching, which also depended on the added element, suggest different corrosion resistance among the three alloys.

KEYWORDS

Spheroidal graphite cast iron;
Nickel;
Cobalt;
Microstructure;
Optical microscopy;
SEM;
XRD.

INTRODUCTION

Cast iron is a rather old and well-known material family. Very numerous works have been carried out about these carbon-rich iron alloys over many decades, and there are even a lot of general books devoted to them[1-7]. One of the latest particularly important developments, even if it occurred in the middle of the last century, is the appearance of a spheroidal shape for graphite. Indeed, a long time ago, this pure carbon phase obtained for solidification slow enough was only of the lamellar shape. This was due to the systematic presence of sulphur in the liquid cast iron leaving the bottom part of the blast furnace, come here inside the coke layers devoted to the reduction of the iron oxides in the ore

layers with which the coke layers are alternated. Preliminarily treating the molten cast iron first with CaO or calcium carbide, and second with magnesium blocks or alloys rich in magnesium (FeSiMg powders), and thereafter inoculating the poured cast iron with iron-silicon rare earth powders allows obtaining, if solidification is not too fast, cast irons with graphite particles which are not flakes but spheroidal nodules. This graphite shape is very interesting for numerous applications for which a not too expensive iron base alloy must be shaped by foundry and own high resistance in traction.

Additions of various other elements than iron, silicon and carbon may be done in spheroidal graphite cast irons (SG cast irons), such as molybdenum for example for more easily obtaining martensite by quenching. But such additions are usually done in rather small quantity. In this work it was attempted to obtain SG cast irons with significant amounts, either in nickel or in cobalt, by re-melting SG cast iron with nickel or with cobalt. Re-melting a SG cast iron part for incorporating new elements by keeping a spheroidal shape for graphite was successfully done recently in the case of silicon[8,9]. Similar procedure was thus applied here, and the obtained microstructures were characterized.

EXPERIMENTAL

Elaboration of the alloys

An elaboration procedure was inspired by the one which had demonstrated its efficiency for the introduction of supplementary silicon[8] was here thought and applied. First a part of the same spheroidal graphite cast iron ingot as in[8] (industrial provenance) was cut (weight about 20g). Since it was found that this industrial ingot contains about 3.5 wt.%C and 2.5 wt.%Si, supplementary 20 grams of new charge was prepared from pure elements: M, C and Si, with M being either Co or Ni. The targeted C and Si contents for these new 20g of future alloy were the same as the one of the industrial ingot. The 20g of industrial SG iron and the 20g of mix of pure elements were thus melted together in the water-cooled copper crucible of a CELES furnace, under about 400 mbars of pure Argon. The wished thermal cycle (1 min at 2.5 kV then 1 min at 3.5 kV) inspired by[8,9] was finally not applied since the added graphite parts were not able to enter the obtained molten alloy and remained on the periphery of the levitating molten ball. Another one was thus applied: 1 minute at 2.5 kV, increase in voltage up to more than 5kV and dwell at this voltage until the main part of graphite was really incorporated in the molten alloy. The decrease in voltage and the rather rapid cooling rate were the same as in[8].

To finish one must add that what is described above for obtaining 40g-weighing ingots of {3.5 wt.% C and 2.5 wt.% Si}-containing cast irons (with a spheroidal shape wished for graphite): on one hand based on Fe and Co in equal quantities, and on the other hand based on Fe and Ni in equal quantities too. It was also applied to obtained a third alloy, with Fe brought by the industrial cast iron and supplementary Fe added as for Co or Ni, for obtaining an alloy devoted to comparison. This latter one was elaborated following exactly the same route as for the two first cast irons (with Co and with Ni).

Ingots' cutting and samples' machining

The obtained ingots were first immersed in a liquid mix of cold resin system (82% CY230 resin and 18% HY253Hardener closely mixed together) in order to obtain a cylindrical mounted ingot much easier to handle then cut. This one was cut using a Buehler Abrasimet Delta metallographic saw to obtain parts for the metallographic characterization and parallelepipeds devoted to the compression tests.

Metallographic characterization

The parts prepared for the metallographic characterization were imbedded in the same cold resin system as mentioned above, ground with SiC papers whose grade increased from 120 to 4000. After ultrasonic cleaning, polishing was done using a textile disk supplied in 1µm alumina or diamond particles.

The mounted and polished samples were first observed using a Olympus optical microscope (BX51 model) equipped with a digital camera (ToupCam) driven with a software (ToupView), to study the graph-

ite shape. Thereafter a Nital etching was applied to observe the metallic matrix (immersion in an {ethanol-4% HNO_3} etchant for about 10 seconds, at room temperature), using the same microscope.

The same samples were also observed by Scanning Electron Microscopy (SEM) using a JEOL JSM 6010LA apparatus equipped with an Energy Dispersion Spectrometry (EDS) device. This was essentially to control the global chemical compositions of the obtained ingots and to specify the chemical composition of the matrix. However it was verified if more details concerning the matrix were visible, to complete the observations done by optical microscopy.

X-Ray Diffraction characterization of the microstructure was also performed using a Philips X'Pert Pro diffractometer (anticathode of copper, K_α transition of Cu with wavelength: 1.5406 Angströms), and the generated files were analyzed using the EVA software.

RESULTS AND DISCUSSION

Optical microstructure observations

Six micrographs were taken per alloy: two at different magnification on three distinct zones, without any etching or after in an etched state (etchant: Nital 4). They are displayed in Figure 1 (not etched) and Figure 2 (etched) for the cast iron containing as cobalt as iron (noted "CoFe"), in Figure 3 (not etched) and Figure 4 (etched) for the cast iron containing as nickel as iron (noted "NiFe"), and in Figure 5 (not etched) and Figure 6 (etched) for the cast iron containing only iron (noted "FeFe"). The observations which can be done about the graphite structures and the matrix among the three locations in each alloy are:

"CoFe" (Co=Fe + 3.5C + 2.5Si):

Before etching (Figure 1): rather heterogeneous microstructure, coarse flake graphite (rosettes) and much finer lamellar graphite, presence of matrix dendrites

After etching (Figure 2): globally no result for this etching, except some rare and small pale brown areas in the matrix far from the graphite lamellae

"NiFe" (Co=Fe + 3.5C + 2.5Si):

Before etching (Figure 3): rather heterogeneous microstructure, coarse flake graphite (plates) and more or less finer lamellar graphite, no dendrites

After etching (Figure 4): no modifications

"FeFe" (Co=Fe + 3.5C + 2.5Si):

Before etching (Figure 5): more homogeneous microstructure, more or less fine compact graphite particles (neither lamellar nor nodular) and more or less finer lamellar graphite, matrix dendrites with curious shapes

After etching (Figure 6): seemingly ferrite in the areas where are dispersed the graphite particles, pearlite in the dendrites

In the three cases it clearly appears that the initial spheroidal shape of graphite was unfortunately not kept. Instead, the obtained graphite was a little particular (lamellar but with a broad range of size, plate graphite…= depending on the new alloy base. But the addition of Co and Ni in the two first alloys maybe induced an increased resistance of the alloys against the chemical attack by Nital.

Electronic microstructure observations

When observed with the SEM in Back Scattered Electrons (BSE) mode, the microstructures are note really better visually characterized, as seen in Figure 7 for three locations in the "CoFe" alloy, Figure 8 for the "NiFe" alloy and Figure 9 in the "FeFe" alloy. But the chemical compositions were specified by full frame EDS analysis at ×250 and by spot EDS analysis in the matrix for the "CoFe" alloy, the "NiFe" alloy and the "FeFe" alloy (TABLE 1). Globally, the contents in Co and Fe in the "CoFe" alloy (full frame or matrix) are very similar to one another, this demonstrating that the re-melting of the industrial cast iron with the additional synthetic alloy was total, and then the elaboration of a {Co=Fe}-based grey cast iron was successful. The same remark can be done for the "NiFe" alloy (and of course of the "FeFe" alloy). In contrast it seems that the silicon content is closer to 2 wt.% than to the targeted 2.5 wt.%. It is possible that the elaboration route induced a loss in silicon, despite the inert atmosphere in which melting was achieved.

XRD results

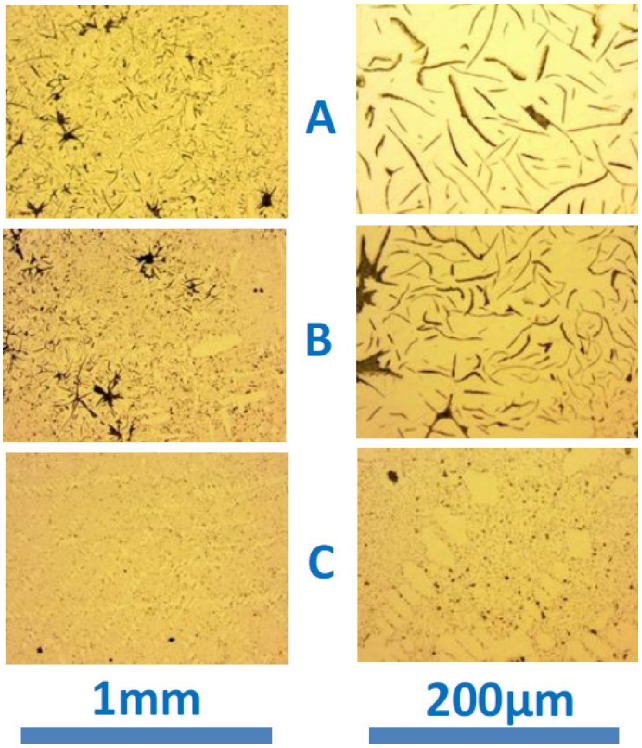

Figure 1 : Graphite structure (without etching) of the "CoFe" cast iron as observed at two magnifications in three distinct zones ("A"," B" and "C")

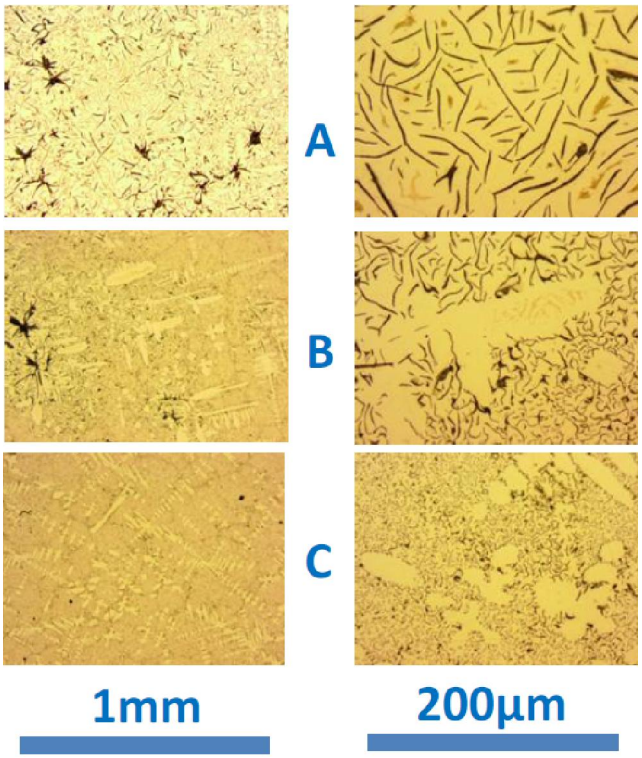

Figure 2 : Matrix structure (after Nital etching) of the "CoFe" cast iron as observed at two magnifications in three distinct zones ("A"," B" and "C")

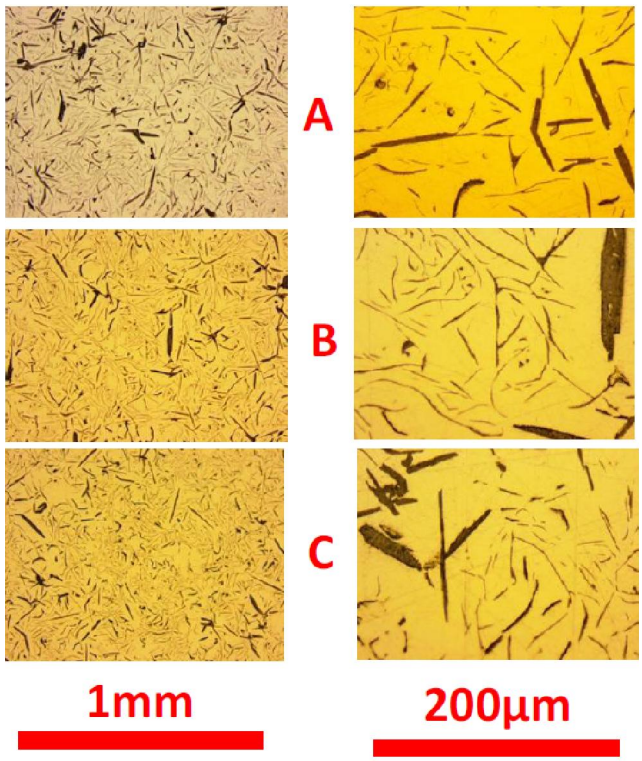

Figure 3 : Graphite structure (without etching) of the "NiFe" cast iron as observed at two magnifications in three distinct zones ("A"," B" and "C")

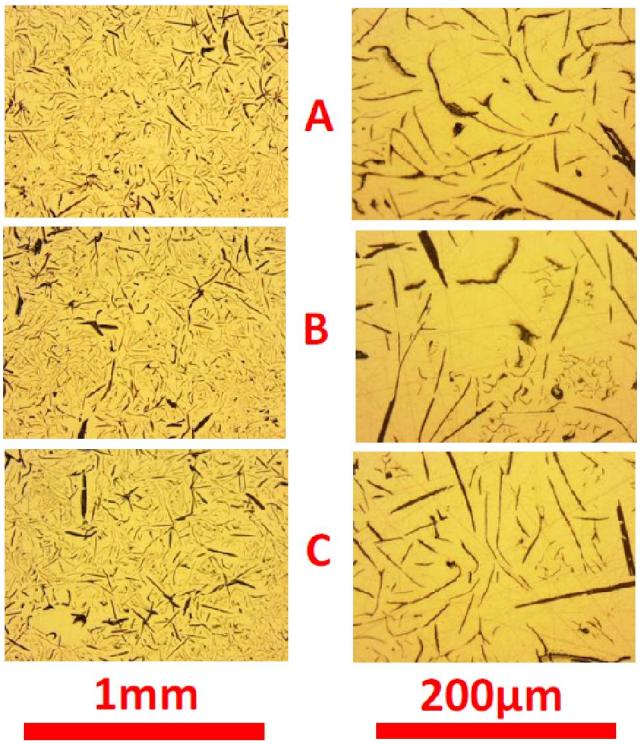

Figure 4 : Matrix structure (after Nital etching) of the "NiFe" cast iron as observed at two magnifications in three distinct zones ("A"," B" and "C")

X-Ray Diffraction was performed on the three samples. The obtained diffractograms are presented

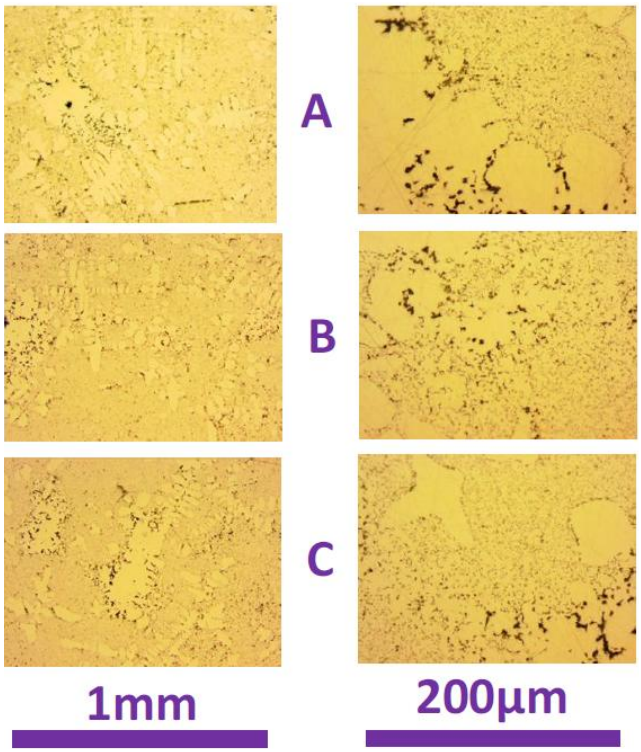

Figure 5 : Graphite structure (without etching) of the "FeFe" cast iron as observed at two magnifications in three distinct zones ("A"," B" and "C")

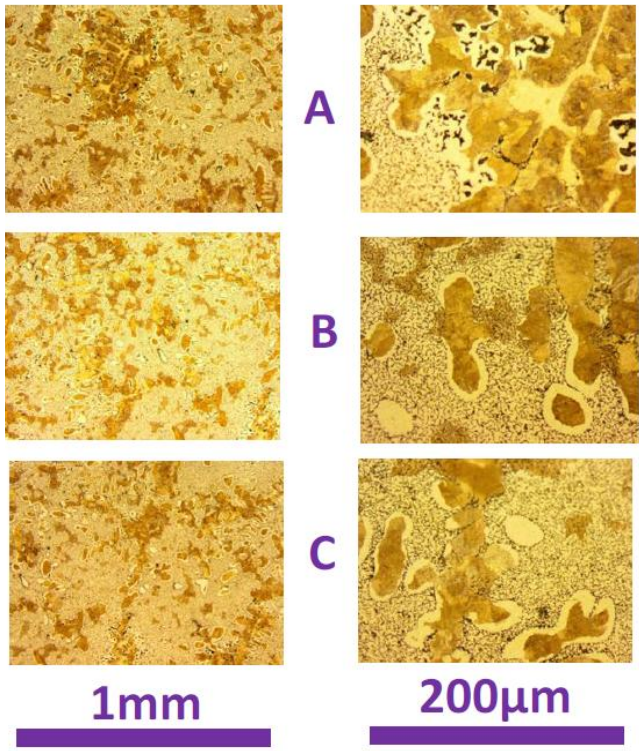

Figure 6 : Matrix structure (after Nital etching) of the "FeFe" cast iron as observed at two magnifications in three distinct zones ("A"," B" and "C")

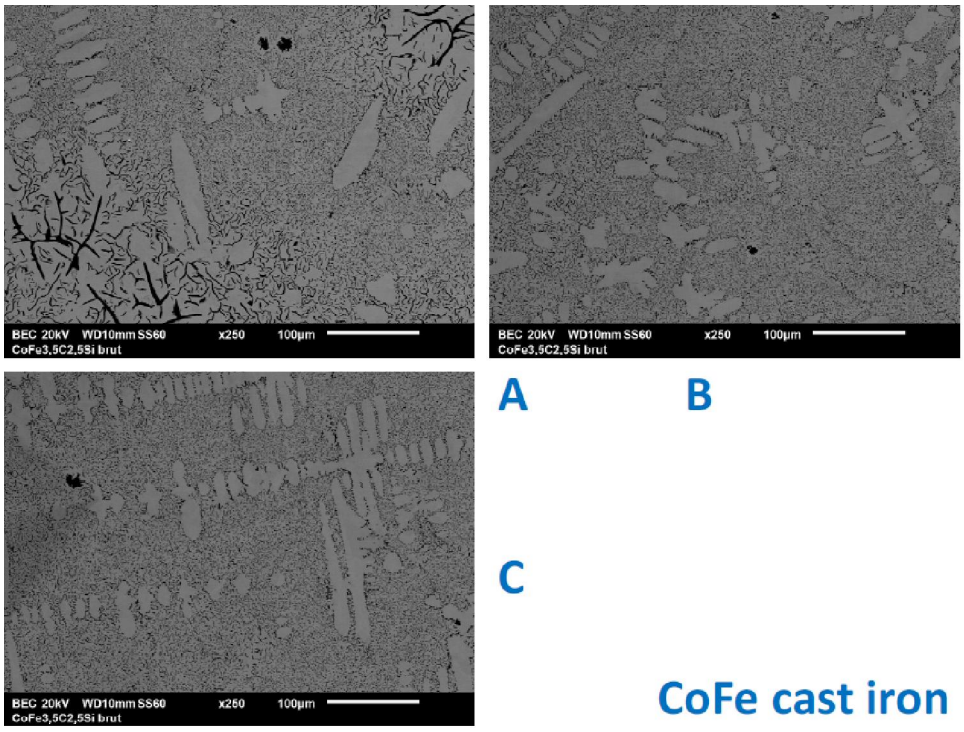

Figure 7 : Microstructure of the "CoFe" cast iron as observed with the SEM (BSE mode) in three distinct zones ("A"," B" and "C")

in Figure 10 for the "CoFe" cast iron, in Figure 11 for the "NiFe" one and in Figure 12 for the "FeFe" one.

It seems that the matrix in the "CoFe" cast iron (Figure 10) is essentially Body Centred Cubic

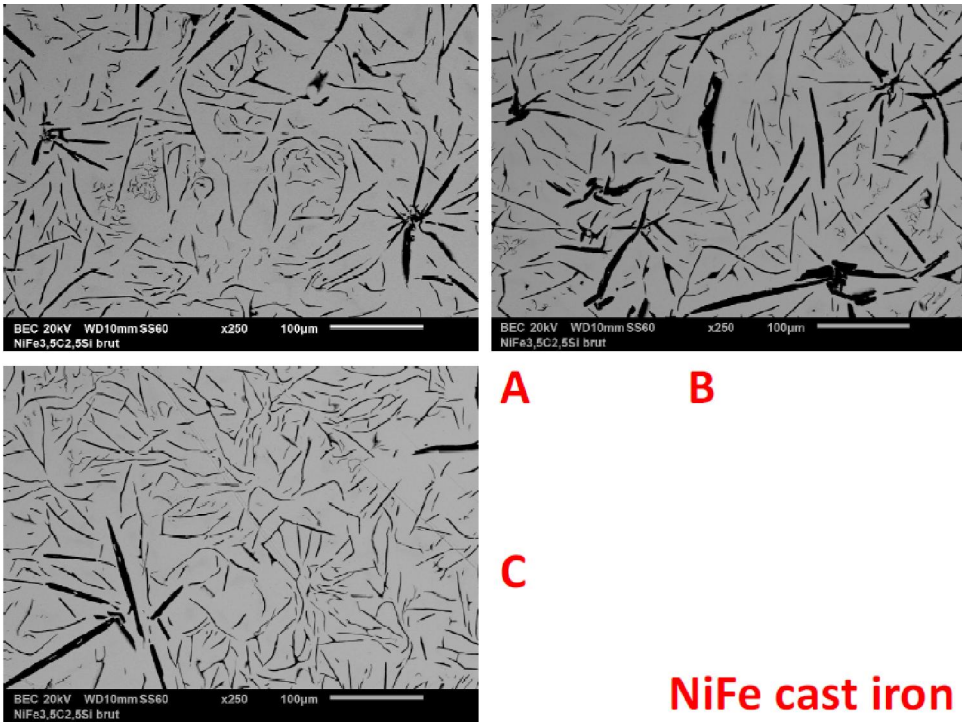

Figure 8 : Microstructure of the "NiFe" cast iron as observed with the SEM (BSE mode) in three distinct zones ("A"," B" and "C")

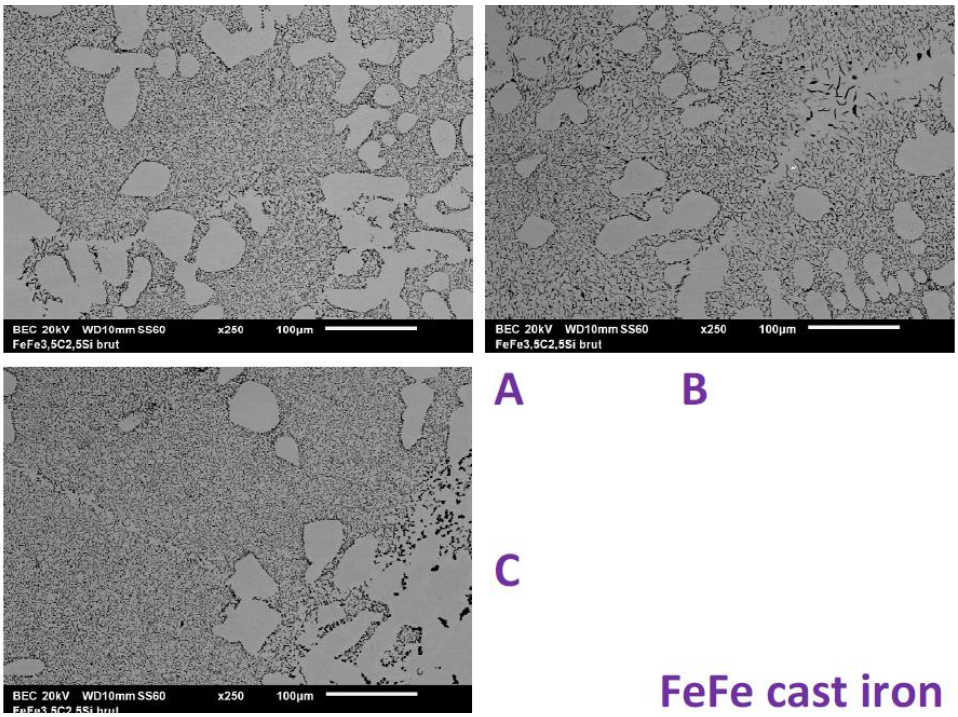

Figure 9 : Microstructure of the "FeFe" cast iron as observed with the SEM (BSE mode) in three distinct zones ("A"," B" and "C")

(BCC), even if some peaks may correspond to a Co_3Fe_7 cubic compound. Graphite seems to be detected too, as in the two other alloys. The "NiFe" cast iron is essentially Face Centred Cubic (FCC) and the "FeFe" one logically BCC with also presence of cementite Fe_3C (orthorhombic).

General commentaries

Thus, contrarily with what was found previously

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TABLE 1 : Full frame ("GLOBAL") and spot ("MATRIX") EDS analysis results (from 3 to 7 results leading to an average value and a standard deviation one); carbon excluded (results automatically adjusted by the SEM to 100% without C)

"CoFe" GLOBAL				'NiFe" GLOBAL				"FeFe" GLOBAL			
Si	2.11	±	0.11	Si	2.27	±	0.09	Si	2.16	±	0.25
Fe	49.33	±	0.64	Fe	51.05	±	0.29	Fe	97.43	±	0.44
Co	48.22	±	0.71	Co	0.09	±	0.08	Co	0.27	±	0.12
Ni	0.34	±	0.15	Ni	46.58	±	0.39	Ni	0.15	±	0.15
wt.% (without C)				wt.% (without C)				wt.% (without C			

"CoFe" MATRIX				'NiFe" MATRIX				"FeFe" MATRIX			
Si	1.86	±	0.15	Si	2.00	±	0.19	Si	2.18	±	0.43
Fe	47.89	±	0.92	Fe	50.38	±	0.63	Fe	97.66	±	0.44
Co	49.67	±	1.09	Co	0.05	±	0.11	Co	0.06	±	0.10
Ni	0.57	±	0.15	Ni	47.57	±	0.86	Ni	0.10	±	0.09
wt.% (without C)				wt.% (without C)				wt.% (without C			

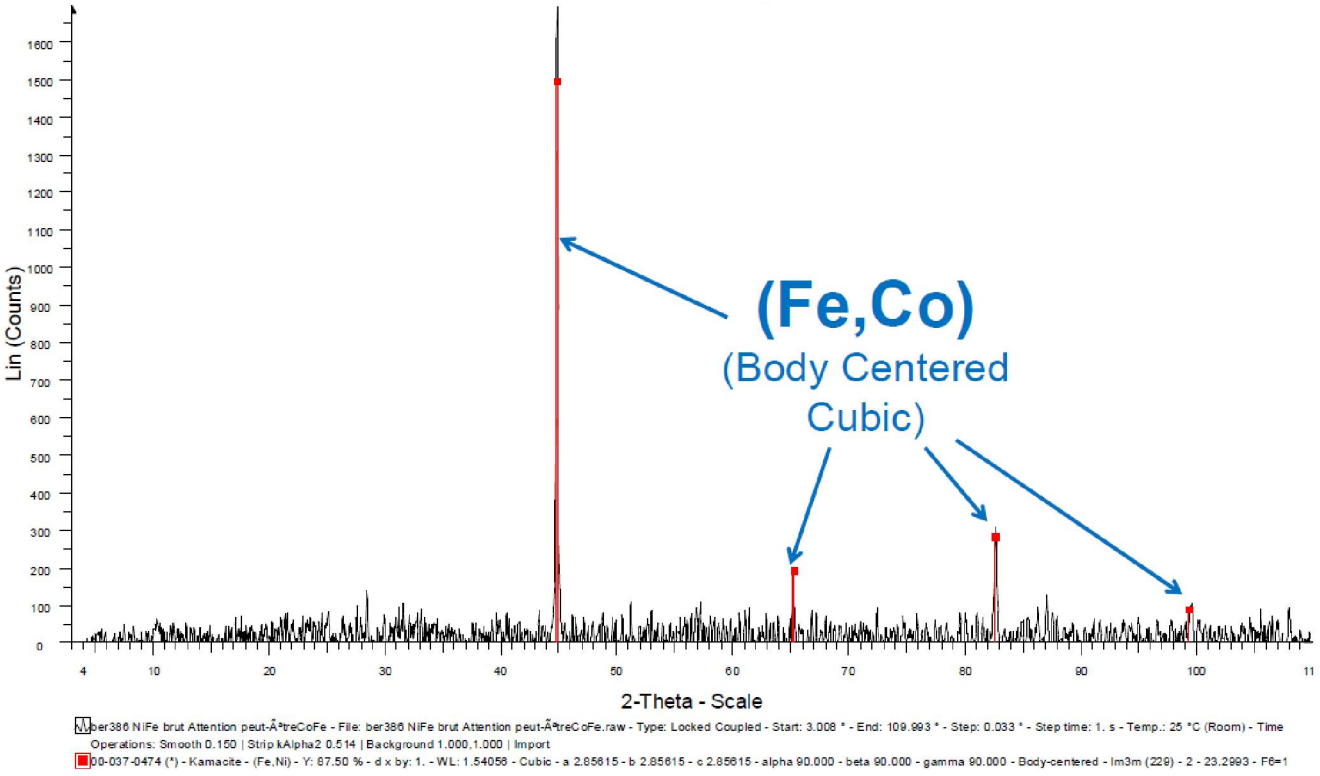

Figure 10 : X-Ray Diffractogram obtained on the "CoFe" cast iron

after re-melting of an industrial spheroidal graphite cast iron for enriching it in silicon[8], none of the obtained cast irons contained nodular graphite. In all cases graphite effectively appeared despite the rather fast cooling then solidification rate, but with a lamellar shape. This can be attributed to the thermal cycle finally applied to ensure the incorporation of the main part of the added graphite parts the dissolution of which was particularly difficult (such problem was not encountered with silicon[8]). The too high temperature and too long dwell duration applied erased what remained of the benefit of the initial desulfuration and spheroidization industrial treatments, while temperature and dwell time were not so high and long in[8] with as result the recovering of the nodular shape of graphite.

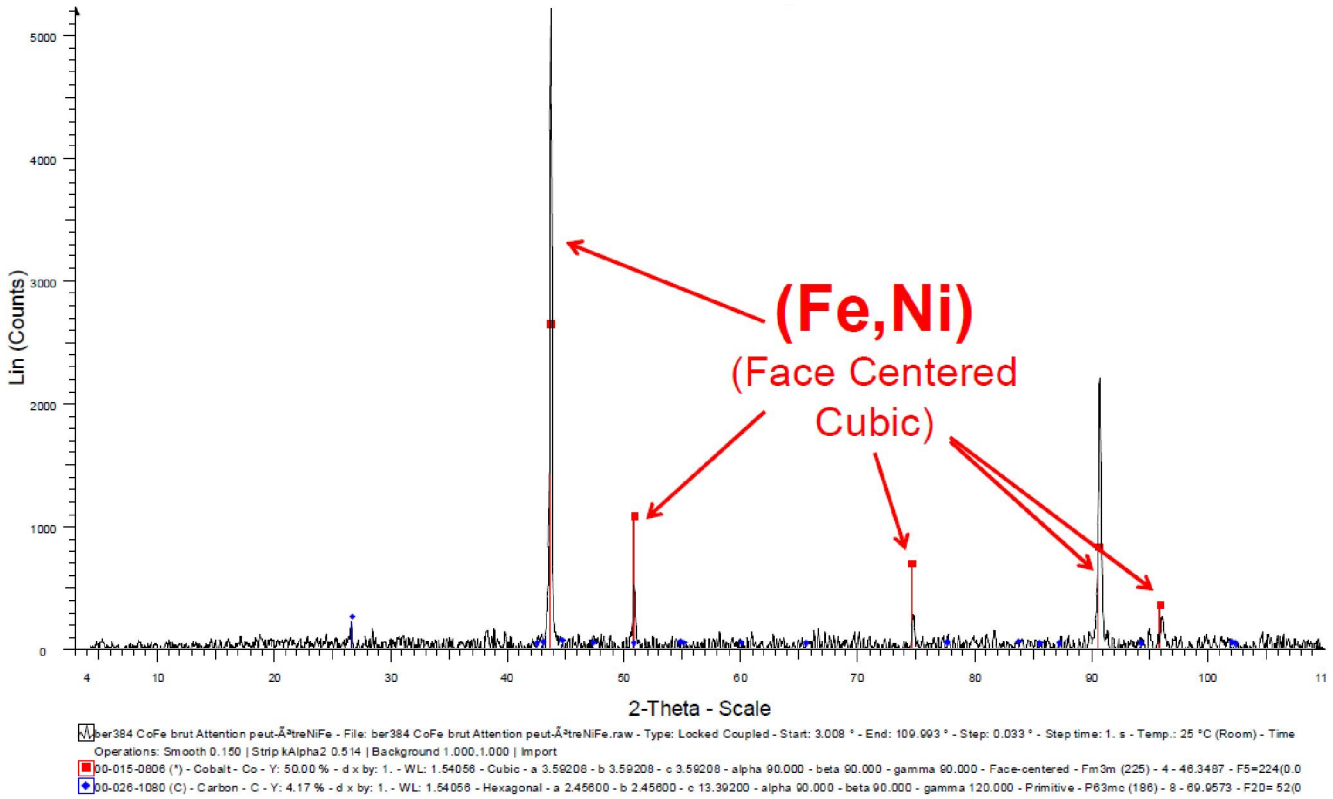

Figure 11 : X-Ray Diffractogram obtained on the "NiFe" cast iron

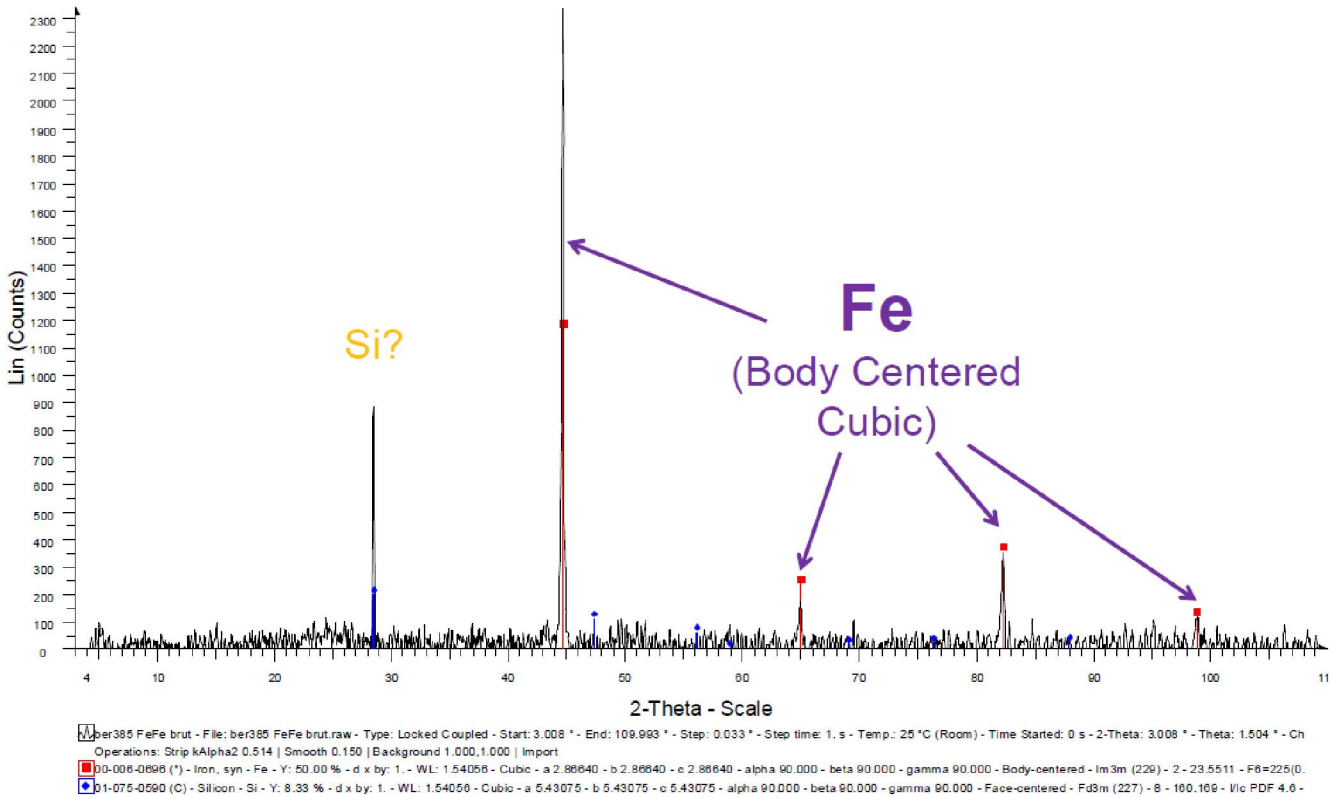

Figure 12 : X-ray diffractogram obtained on the "FeFe" cast iron

Even if graphite was not spheroidal its shape seems depending on the added element: coarse rosettes and fine lamellae for the "CoFe" cast iron, coarse plates and fine lamellae for the "NiFe" one,

and small compact particles for the "FeFe" one. For the latter, the pronounced hypo-eutectic character of the microstructure (numerous dendrites let think to a significant lack in carbon: indeed small graphite parts remained at the ingot's periphery, especially for this "FeFe" cast iron, but also for the two others.

The matrixes of the three alloys are obviously very different from one another. The less surprising one is the ferritic-pearlitic one of the "FeFe" cast iron which corresponds to the metastable Fe-C-Si diagram. The fast cooling in solid state effectively allowed, after a first part in the stable diagram (ferrite), a transition to the metastable one, with as result the change of the eutectoid reaction which results in pearlite. The two other cast iron were either BCC as the "FeFe" cast iron ("CoFe" one) or FCC ("NiFe"). Nital etching reveals only small brown areas in the "CoFe" alloy (the Co_3Fe_7 compound maybe shown by the XRD results?) and seemingly did not affect the "NiFe" one. These two cast irons seem being much corrosion resistant than the "FeFe" one, at least against diluted nitric acid.

CONCLUSION

Thus, the protocol which earlier allowed a silicon enrichment without loss of the nodular shape of graphite of the original industrial cast iron cannot be used for adding high quantities of Co or Ni because of the graphite parts which are compulsory to do not change the C content. The overheating which was applied was fatal for the initial industrial spheroidization treatment. A new protocol must be found and tested now to succeed in Co and Ni-enriching with preservation of the nodular shape of graphite. However the obtained materials are not without any interest and their mechanical properties will be studied now[10].

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