Synthesis and characterization of Fe-containing oxide powders and carbon nanotube-Fe-oxide nanocomposites

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Summary

The goal of this PhD research project was the synthesis and characterization of a number of Fe-containing oxide systems and of the carbon nanotube-nanocomposites obtained by subjecting these oxide materials to a catalytic chemical vapor deposition (CCVD) process using methane or ethylene as carbon source. Various analytical techniques have been applied to characterize the involved samples, such as carbon analysis, BET gas adsorption measurements, X-ray diffraction, thermal analysis (TGA and DTA), transmission and scanning electron microscopy, and Raman and Mössbauer spectroscopy.

First, the synthesis of \(\gamma-(\text{Al}_{1-x}\text{Fe}_x)\text{O}_3\) (\(x = 0.02, 0.05, 0.07\) and \(0.10\)) solid solution powders with high specific surface area (200-230 m\(^2\)/g) by the decomposition of mixed oxinate \([(\text{Al}_{1-x}\text{Fe}_x)(\text{C}_9\text{H}_6\text{ON})_3]\) in air at 800 °C and the potential of these powders as catalytic materials for the synthesis of carbon nanotubes were investigated. The nanocomposite powders prepared by reduction in \(\text{H}_2\text{-CH}_4\) at 1000°C contain carbon nanotubes which are mostly double-walled. However, a fair amount of undesirable carbon nanofibers, hollow carbon particles and metal particles covered by carbon layers were found to be present. By contrast, for nanocomposite powders prepared by reduction in \(\text{N}_2\text{-C}_2\text{H}_4\) at 800°C the carbon deposit is much more abundant and homogeneous and consists in multi-walled carbon nanotubes which however contain a significant proportion of defects.

The syntheses of \(\alpha-(\text{Al},\text{Fe})\text{O}_3\) solid solution powders were performed by the calcination in air of the different \(\gamma-(\text{Al}_{1-x}\text{Fe}_x)\text{O}_3\) solid solutions at high temperatures (~1100 °C). It was for the first time evidenced and proved by different characterization techniques the presence of metallic iron nanoclusters consisting of only a few number of atoms within the \(\alpha-(\text{Al},\text{Fe})\text{O}_3\) solid solution grains. The formation of these nanoclusters is thought to be a consequence of the \(\gamma \rightarrow \alpha\) phase transition which implies structural rearrangement on both the cationic and anionic sublattices.

A comparison of the potential interest of both \(\alpha-(\text{Al},\text{Fe})\text{O}_3\) powders and self-supported foams, as starting materials for the synthesis of carbon nanotubes was performed. Contrary to some expectations, using foams do not lead to an easier reduction of the solid solutions and thus to the formation of more \(\alpha\)-Fe and/or \(\gamma\)-Fe-C potentially active nanoparticles for the formation of carbon nanotubes. There is thus no gain in the quantity of carbon nanotubes. However, using foams strongly favors the selectivity of the method towards single-walled carbon nanotubes (60 % single-
walled and 40 % double-walled carbon nanotubes) compared to what is obtained using powders (5 % single-walled, 65 % double-walled and 30 % multi-walled carbon nanotubes).

The thermal stability in air of a carbon nanotube-Fe-Al₂O₃ nanocomposite powder was studied. The as prepared nanocomposite powder contained α-Fe, Fe₃C, γ-Fe-C, (Al,Fe)₂O₃ and a weakly abundant Fe²⁺ phase as shown by the Mössbauer results. The results have shown that Fe₃C decomposes at relatively low temperatures, while α-Fe and γ-Fe-C remain quite stable up to 670 °C and 850 °C, respectively. The oxidation of the Fe₃C and Fe particles results in the formation of hematite (α-Fe₂O₃).

Information about the composition of the surface layers of the grains that form the carbon nanotube-Fe-Al₂O₃ nanocomposite powders was obtained for the first time from a comparative study of the transmission and emission Mössbauer spectra, the latter ones acquired by the Integral Low-energy Electron Mössbauer Spectroscopy (ILEEMS) technique. Several samples were prepared by reduction of an α-Al₁.₈Fe₀.₂O₃ powder in a H₂-CH₄ atmosphere and changing only the maximum temperature (800 – 1070 °C). The nature of the iron species (Fe³⁺, Fe₃C, α-Fe, γ-Fe-C) is correlated to their location in the material. In addition, carbon nanotubes-Fe-MgAl₂O₄ nanocomposite powders were studied by transmission and emission Mössbauer spectroscopy as well. The studies have demonstrating that emission Mössbauer spectroscopy is a promising tool complementing transmission Mössbauer spectroscopy for the investigation of the location of the metal Fe and iron-carbide nanoparticles in the carbon nanotube-nanocomposite materials.

Finally, iron-substituted mullite powders [(Al,Fe)₆Si₂O₁₃] were prepared by the combustion route and calcined in air (800 – 1400 °C) in order to increase their crystallinity. The thermal treatment resulted in a mixture [(Al,Fe)₆Si₂O₁₃] and α-(Al,Fe)₂O₃. The influence of the calcination temperature of the material on the formation of nanocomposite powders by reduction in H₂-CH₄ at 1050 °C was investigated.
Samenvatting

Het doel van deze doctoraatsstudie omvatte de synthese en karakterisering van een aantal Fe-houdende oxidesystemen en van de (samengestelde) koolstofnanobuisjes-nanocomposietpoeders bekomen door deze systemen te onderwerpen aan een CCVD-proces (catalytic chemical vapor deposition) met methaan of ethyleen als bron voor koolstof. Diverse analytische technieken werden toegepast, zoals analyses voor de bepaling van het koolstofgehalte, BET-metingen ter bepaling van de specifieke oppervlakte, X-straal diffractiemetingen, thermische analyses (TGA en DTA), transmissie en scanning elektronenmicroscopie, raman- en móssbauer-spectroscopie.

In eerste instantie werden γ-(Al\textsubscript{1-x}Fe\textsubscript{x})\textsubscript{2}O\textsubscript{3}-mengpoeders (x = 0.02, 0.05, 0.07 en 0.10) en met hoge specifieke oppervlakte van 200-230 m\textsuperscript{2}/g bereid. De synthese geschiedde door thermische decompositie aan de lucht van de corresponderende (Al,Fe)-oxinate (Al\textsubscript{1-x}Fe\textsubscript{x})(C\textsubscript{9}H\textsubscript{6}ON)\textsubscript{3} bij 800 °C. Het potentieel van die γ-aluminapoeders als katalysators voor de productie van koolstofnanobuisjes werd bestudeerd. De nanocomposietpoeders bekomen door reductie in een (H\textsubscript{2}-CH\textsubscript{4})-atmosfeer bij 1000 °C bevatten naast koolstofnanobuisjes, die hoofdzakelijk van het dubbelwandig type zijn, een aanzienlijke hoeveelheid aan ongewenste koolstofvormen zoals nanovezels, holle koolstofdeeltjes en koolstoflagen die metallische deeltjes omsluiten. Indien daarentegen reductie van de γ-(Al\textsubscript{1-x}Fe\textsubscript{x})\textsubscript{2}O\textsubscript{3}-poeders wordt uitgevoerd bij 800 °C in een (N\textsubscript{2}-C\textsubscript{2}H\textsubscript{4})-atmosfeer, dan blijkt het aantal nanobuisjes ten aanzien van ongewenste koolstofvormen talrijker te zijn en hun morfologie vertoont een hogere graad van homogeniteit. Echter is het merendeel van de koolstofbuisjes meerwandig en structurele defecten zijn overvloedig aanwezig.

In een volgend stadium werden α-(Al,Fe)\textsubscript{2}O\textsubscript{3}-poeders bereid door uitgloeiing in lucht bij relatief hoge temperatuur (~1100 °C) van de voormelde γ-(Al\textsubscript{1-x}Fe\textsubscript{x})\textsubscript{2}O\textsubscript{3}-samenstellingen. Voor het eerst werd vastgesteld en met behulp van diverse karakteriseringstechnieken ondubbelzinnig aangetoond dat bij de transformatie van γ- naar α-almina intragranulaire nanoclusters gevormd worden bestaande uit een klein aantal Fe-atomen. Er wordt aangenomen dat de herschikking van de kationen en anionen die met de γ → α-fasentransitie gepaard gaat aan de basis ligt van de clustervorming.

Vervolgens werd een vergelijkende studie uitgevoerd in hoeverre α-(Al,Fe)\textsubscript{2}O\textsubscript{3}-poeders en α-(Al,Fe)\textsubscript{2}O\textsubscript{3}-schuimen, interessante uitgangsproducten zouden kunnen
Samenvatting

zijn voor de synthese van koolstofnanobuisjes. In tegenstelling tot de verwachtingen blijkt de aanwending van schuimen niet te leiden tot een meer performante reductie, en dus ook niet tot de vorming van een groter aantal nanodeeltjes van $\alpha$-Fe en $\gamma$-Fe-C die geacht worden de katalysators te zijn voor de vorming van de nanobuisjes en zodoende de kwaliteit van die buisjes bepalen. In vergelijking met poeders blijkt het gebruik van schuimen het aantal nanotubes niet te doen toenemen, maar wel de selectiviteit te bevorderen voor de vorming van enkelwandige nanobuizen boven meerwandige, nl. 60% enkelwandige en 40% dubbelwandige, tegenover 5% enkelwandige, 65% dubbelwandige en 30% meerwandige na reductie van de poeders.

De thermische stabiliteit in lucht van een koolstofnanobuis-(Fe-Al$_2$O$_3$)-nanocomposietpoeder werd vervolgens in detail bestudeerd. Met behulp van mössbauerspectroscopie werd vastgesteld dat het betrokken materiaal is samengesteld uit $\alpha$-Fe, Fe$_3$C, $\gamma$-(Fe-C), (Al,Fe)$_2$O$_3$ en, in geringe mate, een Fe$^{2+}$-fase. De resultaten hebben uitgewezen dat Fe$_3$C reeds ontbindt bij een relatief lage temperatuur, terwijl $\alpha$-Fe en $\gamma$-(Fe-C) stabiel blijven tot temperaturen van respectievelijk 670 °C en 850 °C waarna ze oxideren tot hematiet ($\alpha$-Fe$_2$O$_3$).

Voor het eerst werd unieke informatie ingewonnen omtrent de samenstelling van de oppervlaktelagen van de korrels die de bouwstenen zijn van de samengestelde koolstofnanobuisjes-(Fe-Al$_2$O$_3$)-nanocomposietpoeders. Dit geschiedde in een vergelijkend studie van transmissie- en emissiomössbauerspectra, waarbij deze laatste bekomen werden met behulp van Integral Low-Energy Electron Mössbauer Spectroscopy (ILEEMS), die in de eerste plaats gevoelig is voor oppervlaktespecies. Meerdere specimens werden bereid door reductie van een $\alpha$-Al$_{1,8}$Fe$_{0,2}$O$_3$-powder in een (H$_2$-CH$_4$)-atmosfeer waarbij de eindtemperatuur (800 – 1070 °C) werd gevarieerd. Er werd vastgesteld dat de aard van de ijzerspecies (Fe$^{3+}$, Fe$_3$C, $\alpha$-Fe, $\gamma$-Fe-C) gecorreleerd is aan hun locatie in de composietkorrels. Verder werden eveneens een aantal koolstofnanobuisjes-Fe-MgAl$_2$O$_4$-nanocomposietpoeders onderzocht met behulp van zowel transmissie- als emissiomössbauerspectroscopie. Er werd aangetoond dat ILEEMS een veelbelovende techniek is die, in combinatie met de conventionele transmissie-mössbauerspectroscopie, waardevolle informatie verstrekten omtrent de locatie van de metallische ijzerdeeltjes en de ijzer-carbidedeeltjes in de betrokken ijzerhoudende koolstofnanobuisjes-nanocomposieten.

Tenslotte werden Fe-gesubstitueerd mulliet poeders [(Al,Fe)$_6$Si$_2$O$_{13}$] bereid door zeer snelle verbranding van een oplossing van de gepaste Fe-, Al- en Si-zouten met ureum. Om de graad van kristalliniteit van het aldus bekomen poeder te bevorderen, werden stalen ervan uitgegloeid in lucht bij diverse temperaturen in het gebied 800 °C tot 1400 °C. Deze thermische behandelingen resulteerden in de vorming van een
mengsel van (Al,Fe)$_6$Si$_2$O$_{13}$ en $\alpha$-(Al,Fe)$_2$O$_3$. Vervolgens werd de invloed bepaald van de calcinatietemperatuur op de vorming van nanocomposietpoeders die werden gevormd in een (H$_2$-CH$_4$)-atmosfeer bij 1050 °C.
Résumé

Le but de cette thèse de Doctorat est la synthèse et la caractérisation de plusieurs oxydes contenant du fer et de nanocomposites contenant des nanotubes de carbone (NTC), préparés par dépôt chimique catalytique en phase vapeur (CCVD) en utilisant les oxydes comme matériaux catalytiques et le méthane ou l’éthylène comme source de carbone. Différentes techniques analytiques ont été utilisées pour caractériser les matériaux, comme l’analyse élémentaire du carbone, l’adsorption de gaz (méthode BET), la diffraction des rayons X (DRX), l’analyse thermogravimétrique (ATG), l’analyse thermique différentielle (ADT), la microscopie électronique à balayage (MEB) et en transmission (MET), la spectroscopie Raman et la spectroscopie Mössbauer.

Tout d’abord, des poudres de solutions solides $\gamma-(\text{Al}_{1-x}\text{Fe}_x)\text{O}_3$ ($x = 0,02; 0,05; 0,07$ et $0,10$) de grande surface spécifique ($200-230$ m$^2$/g) ont été préparées par décomposition sous air à $800^\circ$C des oxinates mixtes $[(\text{Al}_{1-x}\text{Fe}_x)(\text{C}_9\text{H}_6\text{ON})_3]$. Leur potentiel comme matériaux catalytiques pour la synthèse des NTC a été étudié. Les poudres nanocomposites préparées par réduction sous $\text{H}_2$ et CH$_4$ à $1000^\circ$C contiennent des NTC qui sont principalement biparois. Cependant, une assez forte proportion d’espèces carbonées indésirables (nanofibres, nanoparticules creuses) et de particules métalliques recouvertes de carbone est également observée. En revanche, dans les poudres nanocomposites préparées par réduction sous $\text{N}_2$ et C$_2$H$_4$ à $800^\circ$C, le dépôt carboné est bien plus abondant et homogène, et consiste en des NTC multi-parois contenant cependant une proportion significative de défauts.

La synthèse des poudres de solutions solides $\alpha-(\text{Al},\text{Fe})\text{O}_3$ a été faite par calcination sous air des solutions solides $\gamma-(\text{Al}_{1-x}\text{Fe}_x)\text{O}_3$ à température élevée ($\sim 1100^\circ$C). Différentes techniques de caractérisation ont mis en évidence et démontré, pour la première fois, la présence de nanoclusters de fer métallique ne contenant que quelques atomes au sein des grains de solution solide $\alpha-(\text{Al},\text{Fe})\text{O}_3$. Il est proposé que la formation de ces nanoclusters est une conséquence de la transition de phase $\gamma \rightarrow \alpha$, qui implique un réarrangement structural à la fois sur les sous-réseaux cationique et anionique.

Une comparaison de l’intérêt potentiel des solutions solides $\alpha-(\text{Al},\text{Fe})\text{O}_3$ sous forme de poudres et de mousses autosupportées comme matériaux catalytiques pour la synthèse des NTC a été effectuée. Contrairement à certaines attentes, l’utilisation des mousses ne permet pas une réduction plus poussée des solutions solides et donc ne permet pas la formation de plus de nanoparticules de
Résumé

α-Fe et/ou γ-Fe-C potentiellement actives pour la formation des NTC. On n’obtient donc pas plus de NTC. Cependant, l’utilisation des mousses favorise fortement la sélectivité de la méthode en faveur des NTC monoparois (60% monoparois et 40% biparois) par rapport à ce qui est obtenu à partir des poudres (5% monoparois, 65% biparois et 30% multiparois).

La stabilité thermique sous air d’une poudre nanocomposite NTC-Fe-Al_2O_3 a été étudiée. L’analyse des résultats de spectroscopie Mössbauer a montré que la poudre contient initialement plusieurs espèces du fer : α-Fe, Fe_3C, γ-Fe-C, (Al,Fe)_2O_3 ainsi qu’une phase du Fe^{2+} en faible proportion. Il a été montré que Fe_3C décompose à température relativement basse tandis que α-Fe et γ-Fe-C sont stables jusqu’à respectivement 670°C and 850°C. L’oxydation des particules de Fe_3C et de Fe provoque la formation d’hématite.

Une étude comparative des spectres Mössbauer en transmission et en émission, ces derniers étant obtenus par la technique *Integral Low-energy Electron Mössbauer Spectroscopy* (ILEEMS), a permis pour la première fois d’obtenir des informations sur la composition des couches de surface des grains de poudre nanocomposite NTC-Fe-Al_2O_3. Plusieurs échantillons ont été préparés par réduction d’une poudre α-Al_{1,8}Fe_{0,2}O_3 sous H_2-CH_4, en changeant uniquement la température maximale (800 – 1070°C). La nature des espèces du fer (Fe^{3+}, Fe_3C, α-Fe, γ-Fe-C) a été corrélée à leur localisation dans le matériau. De plus, des poudres nanocomposites NTC-Fe-MgAl_2O_4 ont été également étudiées par spectroscopie Mössbauer en transmission et en émission. Les résultats ont démontré que la spectroscopie Mössbauer en émission est une technique complémentaire prometteuse pour la localisation des nanoparticules de fer et carbure de fer dans de tels matériaux nanocomposites.

Enfin, des poudres de mullite substituée par du fer [(Al,Fe)_6Si_2O_13] ont été préparées par combustion et calcinées sous air à différentes températures (800 – 1400°C) pour accroître leur cristallinité. Ce traitement thermique résulte en la formation d’un mélange de [(Al,Fe)_6Si_2O_13] et de α-(Al,Fe)_2O_3. L’influence de la température de calcination du matériau sur la formation des poudres nanocomposites par réduction sous H_2-CH_4 (20 mol% CH_4) à 1050°C a été étudiée.
Part I

Synthesis and characterization of Fe-containing oxide powders and carbon nanotube-Fe-oxide nanocomposites
Carbon nanotubes (hereafter denoted as CNTs) are one of the most widely investigated nanomaterial (about 15 papers in peer-reviewed journals each day) because they show excellent thermal, electrical and mechanical properties besides that they are very small, hollow and monodimensional.

Single-walled, double-walled and multi-walled CNTs can be produced by the decomposition of a carbonaceous gas at temperatures from 600 °C to 1200 °C on very small transition metal particles. To form catalytic particles that are nanometric in size at the relatively high temperature required for the production of CNTs is a challenge.

In most of the papers available in literature, the CNTs are well-characterized by several techniques, but not a lot of studies have concentrated on the catalytic materials itself. Fe-containing catalysts are one of the most common materials used in the CNTs synthesis. They usually produce CNTs with high efficiency. $^{57}$Fe Mössbauer spectroscopy offers several advantages for the study of Fe-containing compounds. The spectra, and the parameters derived from these, are sensitive to electronic, magnetic and structural characteristics of the probed material and as such, $^{57}$Fe Mössbauer spectroscopy is a useful technique for phase identification and quantification of mixtures of Fe-containing materials. Therefore, $^{57}$Fe Mössbauer spectroscopy technique, applied in the Department of Subatomic and Radiation Physics (NUMAT team) at the University of Ghent (UGent), can accurately characterize iron phases present in the powders before and after formation of CNTs. Although Fe species are often involved in CNTs formation, only relatively few CNT-related studies report on Mössbauer data regarding the species present before and after CNTs synthesis.

The Centre Interuniversitaire de Recherche et d’Ingénierie des Matériaux (CIRIMAT) at Université Paul-Sabatier (UPS) in Toulouse (France) worked out an original and easily done catalytic chemical vapor deposition method. It is based on selective reduction in $\text{H}_2/\text{CH}_4$ atmosphere at high temperature (800-1070 °C) of oxide solid solutions. The metallic nanoparticles are formed in situ, upon reduction,
on the surface of the oxide grains and are therefore of a size adequate to be immediately active for the formation of CNTs.

The goals of this work are to perform a profound investigation of Fe/Al₂O₃ solid solutions and Fe/mullite powders, and the derived CNT nanocomposites by ⁵⁷Fe Mössbauer spectroscopy and to correlate the results with those obtained by other techniques with the aim to obtain information on the formation of the CNTs, thermal stability, and surface composition of the CNT-nanocomposite powders. The other techniques apart from Mössbauer spectroscopy were applied at CIRIMAT laboratory during several exchange visits (totally about six months).

This thesis is structured as follows: in the next chapter a literature survey is given. Chapter 3 contains the methodology applied in this work. In Chapter 4 general conclusions are presented. The second part of this work (Part II) contains the original papers, published or submitted, in which a detailed discussion of the results is given.
In the first part of this chapter a brief introduction of what are carbon nanotubes (CNTs) is given. After details of the catalytic chemical vapor deposition (CCVD) synthesis method of CNTs are presented in Sections 2.2 and 2.3. The last section (2.4) of this chapter concerns the Fe and Fe-carbide species.

2.1 Carbon nanotubes

Iijima reported the observation of multi-walled CNTs in 1991 [1]. Two years later, two independent groups, Iijima and Ichihashi [2] and Bethune et al. [3] reported the growth of single-walled CNTs. Since then many laboratories around the world have been studying these forms of carbon.

The structure of the CNT is a hexagonal lattice (graphene sheet) rolled into a seamless cylindrical tube (Figure 2.1a), sometimes with a cap at each end of the cylinder, such that the two caps can be joined to form a fullerene (Figure 2.1b). These tubes may exist inside other cylinders, with an interlayer distance of ~0.34 nm. A tube that is composed of only one cylinder is named as single-walled CNT (SWNT). A double-walled nanotube (DWNT) is composed of two layers (Figure 2.1c) and multi-walled CNTs (MWNT) are built up by multiple coaxial carbon cylinders. Additionally, some pentagonal and heptagonal defects can cause cylinders to bend, change diameter, or twist.

Figure 2.1 Schematic illustrations of a SWNT without (a) and with caps at each end of the cylinder with half of a fullerene molecule (b), and of a DWNT (c).
A major feature of the CNT structure is the hexagon pattern (honeycomb) that repeats itself periodically in space. As a result of the periodicity, each atom is bonded to three neighboring atoms. This structure is mainly due to the process of \( sp^2 \) hybridization during which three hybrid \( sp^2 \) orbitals are formed at 120° to each other within a plane. This covalent bond, referred to as the \( \sigma \)-bond, is a strong chemical bond. It results in the high stiffness and high strength of a CNT. Additionally, the out-of-plane bond (the \( \pi \)-bond) is relatively weak and contributes to the interaction between the layers in MWNT, and between SWNT’s in SWNT bundles.

The CNTs have diameters in the range between fraction of nanometers and tens of nanometers and lengths up to several tens of micrometers. They are considered as nearly one-dimensional structure according to their high length-to-diameter ratio (\( 10^3 \) - \( 10^5 \)). Moreover, they also have a large external specific surface area (1315 m\(^2\)/g for a SWNT closed and isolated). More information about CNTs can be found in several textbooks [4-9].

The remarkable and unique properties of the CNTs have placed them right among the hottest topics of material science. They exhibit excellent mechanical, thermal and electrical properties. These nanoscale carbon structures are potentially interesting for many applications in various fields such as nanoelectronics, energy storage (Li-batteries, supercapacitors), mechanical reinforcement of composite materials (metallic, ceramic and polymer matrices), removing of electrical charges, detection of gases, electromechanical actuators, etc.

### 2.2 Synthesis of CNTs by CCVD method

The catalytic chemical vapor deposition method is based on the decomposition of a carbonaceous gas on small metal particles. The metal generally used for these reactions are transition metals, such as Fe, Co, and Ni. Additives such as Mo and W are sometimes used. The carbonaceous gas can be either hydrocarbons (\( CH_4 \), \( C_2H_4 \), \( C_2H_2 \) and \( C_6H_6 \), generally mixed with \( H_2 \), \( N_2 \) or \( Ar \)) or CO. The key parameters controlling the formation of CNTs are the CCVD parameters (hydrocarbons species, gas pressure and flow rate, maximum temperature and treatment duration) on the one hand and the catalytic material parameters (nature and content of the transition metal, additives, specific surface area, powder or foam shaping, etc) on the other hand. CCVD has emerged as the main synthesis route for CNTs because it is based on low-cost technology, can be upscaled and the multitude of parameters, as described above, can be fine-tuned and almost always result in reaching the synthesis objectives in terms of yield and selectivity [8]. Moreover, the CCVD method allows the localized and/or oriented formation of CNTs.
2.2.1 Formation of carbon filaments

As reviewed by Monthioux and Kuznetsov [10], the formation of carbon filaments by catalytic decomposition of carbonaceous gases on metal particles has been known since the XIX\textsuperscript{th} century and hollow filaments have first been reported in 1952 [11]. The formation mechanisms have been hotly debated over the years and this subsection concerns the main formation mechanisms that have been reported earlier than the observation of MWNTs by Iijima [1].

In 1976 Oberlin et al. [12] proposed a formation mechanism for tubular carbon filaments. The carbon filament is formed by a catalytic process involving the surface diffusion of carbon species around the metal particle (Figure 2.2a). New metal hydrocarbon species dissociate on its edges and the carbon layers develop by lateral growth following the external surface of the metal particle, thus producing a carbon shell (Figure 2.2b). This growth exerts a force strong enough to remove the catalytic particle from the substrate (Figure 2.2c). When the catalytic particle is covered by carbon layers at the tip, the diffusion stops and the growth ends (Figure 2.2d). The hollow channel in the centre is due to the fact that no carbon supply can reach the back of the particle.

Another explanation for the formation mechanism of the carbon filaments was given by Tibbetts [13]. In this model the author assumed that molecular decomposition and carbon solution occur at one side of the catalytic particle, creating a gradient of concentration in the particle. Consequently, this particle becomes supersaturated and the carbon diffuses to the back face of the particle where precipitation occurs (Figure 2.3).
2 Literature Survey

Figure 2.3 Model for the formation of carbon filaments, showing the inner and the outer diameters and the precipitation interface. After Tibbetts [13].

2.2.2 Formation of CNTs

Yacamán et al. [14] were the first to report that the hollow carbon filaments prepared for decades were indeed similar to Iijima’s MWNTs [1]. Catalyst particles with diameter higher than 10 nm tend to form MWNTs or carbon nanofibers (henceforward called as CNF). Amelinckx et al. [15] have proposed a model directly related to the well-known Vapor-Liquid-Solid (VLS) mechanism [16] which is not really different from earlier mechanisms [12, 13]. A small metallic particle rests on a larger one that acts as a support (Figure 2.4a). The small particle is lifted away from the support by the deposition of graphene sheets formed from carbon diffusion through the catalyst and through the base (Figure 2.4b and c). The outer diameter of the tube becomes equal to the particle size (Figure 2.4d). A layer of graphite covering the small particle and inhibiting further tip growth of the tube (Figure 2.4e). Figure 2.4f shows tubular layers fed by the supporting particle grown beyond the small particle. The small particle is already covered by a graphite layer during the initial stage (Figure 2.4g); further growth occurs by extrusion through the base and diffusion occurs along the graphite surface (Figure 2.4h). Such a mechanism where the catalyst particle is lifted away is known as tip-growth.
Since the diameter of the CNT matches that of the particle, the critical point for the synthesis of SWNTs and DWNTs is the control of the metal particle (catalyst) diameter to a still lower value, i.e., 0.4 - 5 nm. Several hypotheses for the formation of CNTs have been proposed, but an agreement has not yet been reached because the conditions of synthesis are very diverse, and the phenomenon is quite fast and difficult to observe in situ. However, one of the most probable mechanism (the so-called yarmulke mechanism) was proposed by Dai et al. [17] and accounts for the formation of SWNTs and DWNTs. In this model, a nanometric metal particle (Figure 2.5a) contains a very high fraction of surface atoms and the surface energy per atom is very high. An excess of carbon assembles on the metal particle surface to form a graphene cap (the yarmulke) with its edges strongly chemisorbed to the metal (Figure 2.5b). Because the basal plane of graphite has an extremely low surface energy (10 – 20 times smaller than most metals), the total surface energy diminishes. Newly arriving carbon will continue to assemble on the surface of the catalyst. There are three places for additional carbon to go:

1) The original surface shell can continue to grow around the particle, which if continued would result in over-coating and deactivation of the catalytic particle (Figure 2.5c).

2) A second cap can form underneath the first, spaced by roughly the interspacing of graphite. As additional caps form, older caps are forced to lift
up by forming a cylindrical tube whose open end remains chemisorbed onto the catalytic particle (Figure 2.5d and e).

3) Carbon can add to the cylindrical section of a growing layer. Once the smallest yarmulke has formed, insertion of a new carbon between the tube edge and the catalytic particle is the best solution, as long as, complete over-coating is avoided (Figure 2.5f).

![Figure 2.5 Schematic illustration of the yarmulke mechanism adapted by Flahaut et al. [18] from the description of Dai et al. [17].](image)

By contrast to the mechanisms described above for carbon filaments and MWNTs, the yarmulke mechanism is a base-growth mechanism with no particle lift-off. Using surface-energy calculations, Hafner et al. [19] have shown that particles over 3 nm in diameter will get fully covered particle (Figure 2.5c) and thus not give rise to the formation of a CNT. The experimental works of CIRIMAT, more particularly concerning the synthesis of DWNTs [18, 20-22], have confirmed the yarmulke mechanism. With the aim to perform a study of the distribution of the number of walls and the diameter of the CNTs, hundreds of high-resolution transmission electron microscopy images were collected for isolated CNTs. It was found firstly that a particle ≤ 5 nm in diameter produced a CNT with one or two walls, and secondly, that in the same sample, the inner diameter of DWNTs was lower than the diameter of SWNTs, giving evidence that the outer wall is the first one as proposed in the yarmulke mechanism. It was further found that metal particles with diameter between 6 and 10 nm are generally covered by carbon layers forming
the so-called nanoencapsulated particles and that still larger particles produced MWNTs. Furthermore, very large particles lead to the formation of carbon CNF or nanocapsules.

2.3 Synthesis of CNT-nanocomposite powders by the method developed by CIRIMAT

There are two main methods to prepare the catalytic material. The most common one [17, 23] is the impregnation of a powder substrate with a solution of a transition metal salt. After drying and calcination, one obtains a dispersion of particles of the catalytic metal oxide on the substrate. The so-obtained catalytic material can be used for the CCVD treatment, although most authors apply a pre-reduction treatment in order to first obtain metal particles on which the catalytic decomposition of the carbon source will lead to CNT formation. The main advantage of this method is that it is extremely versatile (you can use any substrate and metallic salt). However, the usual particles size is relatively large, which is convenient for the synthesis of MWNTs only. In order to decrease the size of the metal particles, one has to decrease the metal loading which results in a poor yield of the eventual SWNTs and DWNTs.

To overcome this, the Nanocomposite and Carbon Nanotubes team of CIRIMAT has proposed a method [24] where the metal particles are formed in situ during the CCVD treatment, at a relatively high temperature, by selective reduction of solid solutions powders based on Al₂O₃, MgO, MgAl₂O₄, etc. This method is the one applied for the syntheses of the various CNT-nanocomposite powders presented in this work and will be discussed in this section. Note that nanocomposite powders were obtained on purpose in order to further prepare dense nanocomposite materials with very homogeneous CNTs dispersions. However, for CNT-metal-MgO powders, the MgO matrix and most of the metal catalyst can be easily dissolved by soaking the powder in an aqueous solution of a non-oxidative acid such as HCl in mild conditions (room temperature, diluted HCl), thus allowing the preparation of a suspension of undamaged CNTs [25].

The method is based on the synthesis of a catalytic material consisting in an oxide solid solution containing transition-metal ions such as Fe³⁺, Fe²⁺, Co²⁺ and Ni²⁺, for example (Al₁₋ₓFeₓ)₂O₃, Mg₁₋ₓMₓAl₂O₄, Mg₁₋ₓMₓO with M = Fe, Co, Ni [25-28]. Because of the very homogenous dispersion of the transition-metal ions into the oxide solid solution, it is possible to produce very small catalytic metal particles by the selective reduction in a H₂/CH₄ at the high temperature required for the decomposition of hydrocarbon (typically 1000°C for CH₄). The method is schematically described in Figure 2.6.
Figure 2.6 Illustration of the formation of the CNT-nanocomposite-metal oxide powders by the CIRIMAT method where the metal particles are formed in situ during the CCVD treatment.

The metallic nanoparticles formed upon reduction on the surface of the oxide grains are active for the catalytic decomposition of CH$_4$ and have a size adequate for the formation of CNTs. The metal-oxide powder grains are densely covered by a network of CNTs which are very long (up to 100 µm) and flexible (Figure 2.7) and tend to form small bundles along their length.

Figure 2.7 SEM image of a CNT-Fe-Al$_2$O$_3$ nanocomposite powder (a); higher magnification image of the CNT network showing flexible filaments (b) [24].

As mentioned above in the presentation of the yarmulke mechanism, the presence of metal particles with a diameter too high for the formation of CNTs will result in
the presence of undesirable carbon species such as CNF, bamboo filaments, ribbons, carbon layers encapsulating catalyst particles and carbon particles (CP). Typical SEM and high-resolution TEM images of these carbon species are shown in Figure 2.8 and 2.9.

**Figure 2.8** Typical SEM images showing bamboos, CNFs, ribbons and carbon particles [29].

Tremendous efforts by the same group of researchers have been devoted to improving the synthesis of CNTs, i.e., to increase the CNT quantity and the carbon quality (CNT versus other carbon species) and to obtain a high selectivity on the number of walls, with a special emphasis on SWNTs and DWNTs. Note that using catalytic materials in the form of foams, as opposed to powders, allows a significant increase in the production of CNTs and favors the formation of SWNTs over DWNTs, although the exact reason for this is not fully explained yet [22, 30].

In the following, we will review the main results obtained with (Al$_{1-x}$Fe$_x$)$_2$O$_3$ powders. The effects upon the obtained CNTs-oxide nanocomposite powders of the various parameters related to the catalyst material as well as parameters related to the reduction treatment have been systematically investigated: iron content [31],
allotropic form and specific surface area of the solid solution [26, 32], composition of the H₂/CH₄ atmosphere [33], reduction temperature Tᵣ [21], and time spent at Tᵣ [18].

Figure 2.9 Typical high-resolution TEM images of (a) an bamboo; (b) CNF; (c) a filament containing a metal particle; and (d) a metal particle encapsulated by carbon layers [34].

The influence of the metal content on the synthesis of CNT-Fe-Al₂O₃ nanocomposite powders has been studied by Peigney et al. [31]. The nanocomposite powders were prepared by the reduction of α-(Al₁ₓFe₉ₓ)₂O₃ solid solutions with various amounts of Fe (x = 0.02, 0.05, 0.1, 0.15 and 0.2). The authors found that the highest quantity of CNTs was obtained using α-Al₁.8Fe₀.2O₃ as the catalytic material, i.e. the maximum Fe amount (x = 0.1) allowing to retain the monophase solid solution. By contrast, an increase in Fe content (>0.1) induced a phase partitioning and the formation of mixtures of Al₂O₃- and Fe₂O₃-rich solid solutions. The Fe₂O₃-rich (hematite) particles produce upon reduction too large Fe particles, which result in the formation of nanofibers, CNTs with large diameters or end up encapsulated by carbon layers.

Laurent et al. [26] found it necessary to use a stable α-Al₁.8Fe₀.2O₃ solid solution rather than amorphous- or η- Al₁.8Fe₀.2O₃ compounds as starting powder in order to
obtain carbon essentially in the form of CNTs. The crystallization of these latter compounds during the reduction provokes the entrapment of carbon within the grains. Laurent et al. [32] prepared α-Al_{1.8}Fe_{0.2}O_{3} by calcination between 1025 and 1100 °C and the obtained powders were reduced in a H_{2}-CH_{4} gas mixture at high temperature. Calcination at only 1050 °C or 1025 °C resulted in an α-Al_{1.8}Fe_{0.2}O_{3} with a higher specific surface area. It was observed by these authors that the high specific surface area is beneficial to both the quantity and the quality parameters of the nanocomposite powders prepared from the α-Al_{1.8}Fe_{0.2}O_{3} solid solution. By contrast, a higher specific surface area arising from a lower grain size (after some grinding for example) is not beneficial because the better packing of the solid solution powder hampers the formation of the CNTs.

Peigney et al. [33] have investigated the influence of the composition of H_{2}-CH_{4} gas mixtures (range 0 to 45 mol% CH_{4}) on the synthesis of CNT-Fe-Al_{2}O_{3} nanocomposite powders prepared by selective reduction of α-Al_{1.9}Fe_{0.1}O_{3}. Methane concentrations ranging between 9 and 18 mol% gave the best results.

Peigney et al. [21] produced SWNTs and DWNTs with an average diameter close to 2.5 nm by the reduction of an α-Al_{1.8}Fe_{0.2}O_{3} powder in H_{2}-CH_{4} atmosphere applying different reduction temperatures $T_r$ (in the range between 800 °C to 1070 °C). The authors found that increasing the $T_r$ increases the reduction yield and thus favors the formation of surface metal particles, thus producing more CNTs. Flahaut et al. [18] reported the influence of time spent at $T_r$ on synthesis of CNTs. The authors observed that increasing the dwell at the maximum temperature reached during the reduction process results in the production of CNTs with more walls.

At the end of the nineties, the research collaboration between CIRIMAT and NUMAT (at University of Ghent) on the study of carbon-free metal-oxide nanocomposites was therefore extended to such compounds. Indeed, $^{57}$Fe Mössbauer spectroscopy has shown to be a useful, complimentary technique to examine the Fe-containing CNT-nanocomposite powders as well as the starting oxides. This technique, being specific for Fe phases, was believed to be able to provide unique formation about the Fe-containing particles. Various oxide solid-solutions such as (Al_{1-x}Fe_{x})_{2}O_{3}, Mg_{1-x}M_{x}Al_{2}O_{4}, Mg_{1-x}M_{x}O, Zr_{1-x}M_{x}O_{2} with $M = \text{Fe, Co, Ni}$, were considered [21, 35-39]. Common to all CNT-Fe-oxide nanocomposite powders investigated by Mössbauer spectroscopy, is the presence of three characteristic Fe-phases: $\alpha$-Fe, Fe_{3}C (cementite) and a $\gamma$-Fe-C phase [21, 36, 40-44]. A lot of work was devoted to correlate the identified Fe-phases to the carbon species in the CNT-Fe-oxide nanocomposite powders. One of the conclusions at the time was that the particles active for the formation of CNTs are probably Fe-C alloys but are detected as Fe_{2}C in post-reaction Mössbauer spectroscopy analysis. More details about these three Fe-phases will be given in the next section.
2.4 About Fe and Fe-carbide species

Iron has three allotropic forms, known as alpha, gamma and delta. In ordinary temperature and pressure conditions, iron crystallizes in the body-centered cubic (bcc) crystal structure (α-Fe). Between 912 °C and 1394 °C, it crystallizes in the face-centered cubic (fcc) structure (γ-Fe), and between 1394 °C and 1538 °C iron has again a bcc structure (δ-Fe).

Because both α-Fe and δ-Fe are bcc, they are identical in structure but are differentiated by name: α-Fe (ferrite) is of great practical importance, while δ-Fe is relatively unimportant. In earlier times it was believed that another phase, β-Fe, existed but this was shown to be α-Fe above its Curie temperature (770 °C). The α-Fe transforms from ferromagnetic to paramagnetic state at 770 °C while maintaining the bcc structure. The old denomination β-Fe corresponding to paramagnetic bcc iron is no longer used. At room temperature bulk ferromagnetic α-Fe is characterized by a sextet of well-known Mössbauer parameters: \( B_{hf} = 33.0 \, \text{T} \), \( \delta = 0.00 \, \text{mm/s} \) and \( 2Q_{eq} = 0.00 \, \text{mm/s} \). Paramagnetic α-Fe is characterized by a singlet and no quadrupole splitting is detected.

The Fe-C binary [45] system is usually described in terms of Fe and the metastable carbide Fe₃C (cementite), as well as in terms of Fe and stable graphite. Carbon is soluble to only a very small amount in α-Fe (up to about 0.022 wt.% at 727 °C. On the other hand, γ-Fe has a much higher solubility for carbon than α-Fe (up to 2.14 wt.% at 1147 °C) due to the presence of large interstices in the fcc structure. The temperature of 727 °C and a carbon concentration of 0.76 wt.% is a eutectoid decomposition in the Fe-C diagram, where γ-Fe transforms to a mixture of α-Fe and Fe₃C. Several works on CNT-nanocomposite systems prepared by CCVD method [21,33,37,41] reported the presence of γ-Fe-C nanoparticles on these powders besides others Fe and Fe-carbide nanoparticles. The spectrum of the γ-Fe-C phase was composed by a singlet with an isomer shift \( \delta \) of \(-0.12 \, \text{mm/s}\) at 295 K. Coquay et al. [40] obtained a Mössbauer spectrum of a CNT-nanocomposite powder at 4.2 K and observed that the present γ-Fe-C showed an antiferromagnetic coupling. The spectrum was fitted using a weak-hyperfine-field of \(-1.8 \, \text{T}\).

More than ten iron-carbides are mentioned in the literature [45]. Among them, Fe₃C being the most common and stable one at room temperature. It has an orthorhombic unit cell and two inequivalent crystallographic Fe-sites [46, 47], which are magnetically and electronically very similar. Bi et al. [48] have shown the differences between the Mössbauer parameters of the two Fe-sites of Fe₃C which increase with decreasing temperature (Table 2.1). The authors have performed Mössbauer measurements between 12 K and room temperature on bulk Fe₃C and
Fe$_3$C nanoparticles (as small as 5 nm). Interesting, no superparamagnetism was observed even for the smallest particles measured at room temperature.

**Table 2.1** Room temperature and 12 K Mössbauer parameters for nanoparticle and bulk Fe$_3$C [48].

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Nanoparticle Fe$_3$C</th>
<th>Bulk Fe$_3$C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$B_{hf}$ (T)</td>
<td>$2\delta_Q$ (mm/s)</td>
</tr>
<tr>
<td>300</td>
<td>Fe (site i)</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>Fe (site ii)</td>
<td>19.8</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>20.4</td>
</tr>
<tr>
<td>12</td>
<td>Fe (site i)</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td>Fe (site ii)</td>
<td>23.7</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>24.6</td>
</tr>
</tbody>
</table>

Note: $B_{hf}$: hyperfine field; $\delta$: isomer shift; $2\delta_Q$: quadrupole shift
Methodology

3.1 Synthesis procedures

All details about the synthesis procedures used for the catalytic materials as well as for the CNT nanocomposites by reduction of these catalytic materials are outlined in the papers that are reproduced in Part II. The synthesis flowcharts are briefly presented in what follows.

The procedure for the synthesis of the mixed oxinates powders, \((\text{Al}_{1-x}\text{Fe}_x)(\text{C}_9\text{H}_6\text{ON})_3\), is shown in Figure 3.1 (see paper I).

**Figure 3.1** Flow-chart showing the synthesis of the \((\text{Al}_{1-x}\text{Fe}_x)(\text{C}_9\text{H}_6\text{ON})_3\) oxinate powders.
The preparation of the $\gamma-(\text{Al}_{1-x}\text{Fe}_x)\text{O}_3$ powders by decomposition of the $(\text{Al}_{1-x}\text{Fe}_x)(\text{C}_9\text{H}_6\text{ON})_3$ powders and the subsequent synthesis of CNT-Fe-Al$_2$O$_3$ nanocomposites by reduction of the former compounds are shown in Figure 3.2 (see paper I).

Figure 3.2 Flow-chart of the CNT-Fe-Al$_2$O$_3$ nanocomposites synthesis from $\gamma-(\text{Al}_{1-x}\text{Fe}_x)\text{O}_3$ powders.

$\alpha-(\text{Al}_{1-x}\text{Fe}_x)\text{O}_3$ oxide powders were prepared by heating the $\gamma-(\text{Al}_{1-x}\text{Fe}_x)\text{O}_3$ solid solutions at high temperatures (1100 or 1120 °C) in air (Figure 3.3). Further, the $\alpha$-powders were used to prepare self-supported $\alpha-(\text{Al}_{1-x}\text{Fe}_x)\text{O}_3$ oxide foams by impregnation of a polyurethane foam with a slurry (oxide plus a dispersant) followed by a calcination at 600 °C. The $\alpha-(\text{Al}_{1-x}\text{Fe}_x)\text{O}_3$ oxide powders and foams were submitted to CCVD treatment to obtain CNT-Fe-Al$_2$O$_3$ nanocomposites as shown in Figure 3.3 (see paper III).
An Fe/mullite powder was prepared by combustion route. After, several batches of the so-obtained combustion powder were calcined in air at selected temperatures between 800 °C and 1400 °C. The obtained powders were used for the synthesis of CNT-Fe-mullite nanocomposites by reduction in H₂-CH₄ gas mixture (Figure 3.4), see paper VII.
3.2 Characterization

Several techniques such as Mössbauer spectroscopy (transmission and emission), X-ray diffraction, specific surface area measurements, carbon analysis, Raman spectroscopy, and scanning and transmission electron microscopy have been intensively used for the characterization of the various samples considered in this research project. All mentioned techniques, except Mössbauer spectroscopy, were
applied in CIRIMAT laboratories (UPS, Toulouse) in collaboration with local research teams. Selected groups of samples have additionally been investigated by Fe K-edge XANES (in collaboration with Dr. S.G. Eeckhout (ESRF Grenoble, France) and Dr. G. Giuli (Dipartimento di Scienze della Terra and INFM, Università di Camerino, Italy).

3.2.1 Mössbauer spectroscopy

Mössbauer spectroscopy is a technique based on the recoil-free emission and subsequent absorption of γ-rays by certain isotopes. The phenomenon of emission of a γ-photon without loss of energy due to recoil of the nucleus (and without thermal broadening) is known as the Mössbauer effect, after R.L. Mössbauer who discovered and explained the effect in 1958. Its unique feature is the production of monochromatic electromagnetic radiation with an extremely narrow energy spectrum, so that it can be used to resolve minute energy differences.

The electromagnetic interactions between the nucleus and the surrounding charge distribution have a significant effect on the nuclear energy levels. Three interactions are of major importance, respectively the electric monopole, the electric quadrupole and the magnetic dipole interaction. In the Mössbauer spectra they give rise to three parameters: the isomer shift $\delta$, the quadrupole splitting $\Delta E_Q$ or shift $\delta_Q$, and the magnetic hyperfine field $B_{hf}$, respectively. Their values are characteristic of the compound being studied and very often can be decisive as to the precise nature of that compound.

In this work two different variants of $^{57}$Fe Mössbauer spectroscopy have been applied. The first one is the transmission technique whereby the 14.4 keV γ-quanta emitted by a standard source and transmitted through an absorber of the investigated material are counted. The energy of the incident γ-quanta as experienced by the absorber nuclei is modulated through the Doppler effect by subjecting the source to a continuously oscillating velocity in a range $-v_0$ to $+v_0$. A Mössbauer spectrum is then obtained by measuring the transmission as a function of the source velocity, which commonly is of the order of several mm/s in the case of $^{57}$Fe. In addition, for many samples emission Mössbauer spectra have been acquired as well. For this purpose use was made of Integral Low-Energy Electron Mössbauer Spectroscopy (ILEEMS). This method counts the low-energy ($< 15$ eV) Auger and shake-off electrons that are emitted by the absorber nuclei, which have been excited by resonant absorption of incident 14.4 keV γ-quanta. Acquisition of data is also performed as a function of source velocity. Emission spectra yield information similar to that obtained from transmission spectra, but the information primarily refers to Fe species present in the top surface layers of the substance being examined.
Transmission Mössbauer spectra were collected at temperatures between 4.2 K and 295 K, whereas ILEEMS spectra were obtained exclusively at 295 K. Accumulation of the data was made in 1024 channels. The spectrometers have been calibrated by collecting at room temperature the spectrum of a standard hematite ($\alpha$-Fe$_2$O$_3$) powder or a standard metallic iron foil. The isomer shifts quoted in this thesis are referenced with respect to $\alpha$-Fe at room temperature. *In-situ* high temperature transmission Mössbauer spectroscopy was applied at selected temperatures between 295 K and 1123 K.

The Mössbauer spectra were generally fitted with Lorentzian line shapes and, where found necessary, some spectra components were described by a model-independent hyperfine field or quadrupole splitting distribution with Lorentzian-shaped elemental spectra (for instance in the case of Fe$_3$C component) [49]. In that case, the hyperfine-parameter values quoted in this thesis refer to maximum-probability values.

### 3.2.2 X-ray diffraction (XRD)

X-ray diffraction involves interaction of electromagnetic radiation with a wavelength ($\lambda$) of around 0.1 nm, with the atoms in the solid. As the distances between the atoms in a crystal structure are comparable with the wavelength of the radiation, crystals can diffract X-rays. The incidence angles ($\theta$), the wavelength of the rays and the lattice spacings ($d_{hkl}$) are related by the Bragg equation:

\[ n\lambda = 2d_{hkl} \sin \theta \]

It is a versatile, non-destructive technique that reveals detailed information about the composition and structure of the crystallized phases present in the materials, allows to calculate lattice parameters of these phases and can also provide information of their degree of crystallinity and on the size of the crystallites.

For identification of crystalline phases, XRD patterns were recorded in the range 10-70° (2\(\theta\)) using a Bruker D4 Endeavor diffractometer equipped with a Cu K\(\alpha\) radiation tube ($\lambda = 1.5406$ Å). Counts were registered every 0.02° (2\(\theta\)).

In order to calculate the cell parameters, XRD patterns were recorded in the range 20-70° (2\(\theta\)) using a Seifert 3003 TT diffractometer equipped with a CuK\(\alpha\) radiation tube. Counts were registered every 0.02° (2\(\theta\)). The cell parameters were calculated by the Rietveld method using the “Fullprof” software.
3.2.3 Thermal analysis

**Thermogravimetric analysis (TGA)**

Thermogravimetric analysis is a technique in which the weight of the sample is monitored versus temperature (or time in isothermal mode) under a specified atmosphere. One should be able to extract information such as adsorbed moisture content, temperature of decomposition/oxidation of a sample or a part of a sample, etc.

TGA was performed to study the decomposition of the oxinates. The analysis was carried out using about 30 mg of each sample in a SETARAM TAG 24 module (simultaneous symmetrical thermoanalyser). The temperature ranged from 25 to 1000 °C, using a constant flow of synthetic air (25 mL/min) and applying a heating rate of 1 °C/min.

In order to study the decomposition/oxidation of a nanocomposite powder, TGA was carried out in the temperature range 25°C - 1300 °C using a constant flow of synthetic air (1.5 l/h) and applying a heating rate of 1 °C/min.

**Differential thermal analyses (DTA)**

DTA is a technique in which the difference in temperature between the sample and an inert reference material is measured as a function of temperature. When the sample and the reference material are heated identically, phase changes and other thermally-induced phenomena in the sample cause a difference in temperature between the sample and reference.

To determine the $\gamma$-(Al,Fe)$_2$O$_3 \rightarrow \alpha$-(Al,Fe)$_2$O$_3$ transition temperatures, DTA were carried out in a Du Pont SDT 2960 equipment on small samples of each powder. The DTA curves were recorded in the range 25°C - 1300 °C, using a flow of synthetic air (100 mL/min) and a heating rate of 10 °C/min. The reference was a powder of $\alpha$-Al$_2$O$_3$.

3.2.4 Specific surface area measurements

The measurement of the specific surface area consists of the determination of the gaseous volume required to form a monolayer of adsorbed gas on the surface of the powder, according to the theory developed by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller (BET method).
The specific surface area (SSA) measurements of the powders were performed in Toulouse (France) using nitrogen gas adsorption at liquid nitrogen temperature in a Micrometrics Flow Sorb II 2300 apparatus. This instrument gives a SSA value from one point (i.e. one adsorbate pressure) and requires calibration. The alumina and mullite powders were outgassed during 30 min in flowing nitrogen at 250 °C. To avoid damage of the nanotubes the CNT-nanocomposite powders were outgassed at 120 °C for 1h in flowing nitrogen. The accuracy of the obtained SSA values is ± 3 %.

3.2.5 Carbon analysis

The carbon content \( [C_n \text{ (wt.%)}] \) in the CNT-nanocomposite powders was measured by flash-combustion method. It consists of a preheating of the powder at 925 °C followed by fast heating at 1800 °C for about 1 s and measuring of the amount of produced CO\(_2\). The accuracy of the measurements is ± 2 %.

3.2.6 Raman spectroscopy

Raman spectroscopy is based on the Raman effect, which is the inelastic scattering of photons by molecules or crystals. This technique is used to study vibrational, rotational, and other low-frequency modes in a system. A laser beam is used to illuminate an area (spot) on the sample under investigation. The scattered radiation produced by the Raman effect contains information about the energies of vibrations and rotations, and these depend on the particular atoms or ions in the material, the chemical bonds between them, the symmetry of the structure, and the physico-chemical environment.

The acquisition of the Raman spectra was realized using a LabRAM 800 Jobin-Yvon spectrometer with a laser wavelength of 632.82 nm.

Two Raman shift ranges are particularly interesting for CNTs characterization:
- Between 100 and 250 cm\(^{-1}\): the peaks correspond to the radial breathing modes (RBM) of the CNT. The position of the peaks is inversely proportional to the CNT diameter [50].
- Between 1250 and 1700 cm\(^{-1}\): two bands are usually observed. The first one (D band) is centered around 1320 cm\(^{-1}\) and is due to the presence of sp\(^3\) carbon. The second one (G band) is centered at approximately 1580 cm\(^{-1}\) and represents the tangential vibration modes in the graphene tube and thus accounts for sp\(^2\) carbon. The ratio between the D and G band intensities (\(I_{DG}\)) offers information on both the carbon quality in the sample (CNTs versus other carbon species) and the quality of the CNTs themselves. An increasing \(I_{DG}\) value corresponds to a higher proportion of sp\(^3\)-like carbon, which is
generally attributed to the presence of disordered carbon or to structural defects within the CNTs or both.

The $I_{D}/I_{G}$ values reported in this thesis are the result of the average of three values obtained in three different areas for each of the samples.

### 3.2.7 Electron microscopy

**Scanning electron microscopy**

Scanning electron microscopy (SEM) is a technique which permits to image the sample surface by scanning it with a high-energy electron beam. Because of the interaction between the beam and the sample, several different signals are produced. Depending on the mode of observation, these signals provide information about the surface composition, topography and porosity. In the case of powders, low- and medium magnification images provide information on the state of agglomeration and on the shape and granulometry of the agglomerates and primary grains. High-magnification, high-resolution images are necessary for the detailed observation of carbon species such as CNTs.

The powders were coated with platinum for observation by field-emission-gun scanning electron microscopy (FEG-SEM). A JEOL JSM 6700F microscope was used. The observations were performed under a tension of 5 kV. The resolution of this apparatus allows to distinguish between CNT bundles and other forms of carbon (such as thick fibers), and also to resolve individual CNTs, thus giving a qualitative representation of the carbon quality and of the CNT quantity in the nanocomposite powders.

**Transmission electron microscopy**

Transmission electron microscopy (TEM) involves a high voltage beam of electrons which is transmitted through a very thin sample, interacting with the electron density in the specimen as the electrons pass through. Images made from the transmitted electron beam are called bright-field images.

Bright-field TEM images were obtained using a JEOL JEM 1011 microscope operated at 100 kV. To quantify the distribution of the number of walls and of the diameter of the CNTs, high-resolution TEM (HRTEM) has been performed using a JEOL JEM 2100F microscope operated at 200 kV (by Mr. L. Datas, CIRIMAT, Toulouse). The magnification and resolution of the apparatus allows to clearly resolve isolated CNTs, so that their number of walls and their diameter can be determined by a direct measurement on the images.
Using a low-light camera allows to capturing images in real time and the direct obtaining of digital images. This is an important advantage when observing CNTs because their sensitivity to the electron beam (vibrations and damages) usually prohibits the use of films that require much longer exposure times.

The powders were slightly sonicated in ethanol to obtain a suitable dispersion without provoking much damage to the CNTs. A few drops of the suspension were subsequently deposited on a holey carbon film attached to a copper grid. Only the CNTs over the holes were observed in order to avoid any interference with the carbon film.
General Conclusions

In this work, the synthesis of (Al,Fe)$_2$O$_3$ and (Al,Fe)$_6$Si$_2$O$_{13}$ powders and of the corresponding CNTs-metal-oxide nanocomposite powders were carried out, with a thorough investigation by $^{57}$Fe Mössbauer spectroscopy, X-ray diffraction, scanning and transmission electron microscopy, Raman spectroscopy, carbon analysis, specific surface area measurements and other complementary techniques.

One of the principle goals of this thesis was to work out a novel route to prepare (Al,Fe)$_2$O$_3$ solid solutions and to study their potential as catalytic materials for the synthesis of CNTs by a CCVD method. It was found that the decomposition of mixed metal oxinates [(Al$_{1-x}$Fe$_x$)(C$_9$H$_6$ON)$_3$] at 800 °C produces $\gamma$-(Al$_{1-x}$Fe$_x$)$_2$O$_3$ powders with high specific surface area (200-230 m$^2$/g), which is an important parameter that may favor the synthesis of CNTs. The calcination in air (1100 or 1120°C) of the metastable $\gamma$-(Al$_{1-x}$Fe$_x$)$_2$O$_3$ powders produced the stable $\alpha$-(Al$_{1-x}$Fe$_x$)$_2$O$_3$ powders with a low specific surface area (5 m$^2$/g). The Mössbauer spectra of the latter solid solutions featured the well-known asymmetry of the doublet representing Fe$^{3+}$ ions substituting for Al$^{3+}$ ions in the corundum lattice, which was resolved for the first time and attributed to the presence of metallic Fe nanoclusters within the oxide grains. The formation of these nanoclusters is suggested to be a consequence of the $\gamma \rightarrow \alpha$ phase transition which implies structural rearrangement on both the cationic and anionic sublattices.

The CNTs prepared by the reduction of $\gamma$-(Al$_{1-x}$Fe$_x$)$_2$O$_3$ precursor powders in H$_2$-CH$_4$ atmosphere at 1000 °C are mostly DWNT but a fair amount of undesirable carbon nanofibers, hollow carbon particles and metal particles covered by graphene layers were observed as well. By contrast, in the nanocomposite powders prepared by reduction in N$_2$-C$_2$H$_4$ at 800 °C the CNTs are much more abundant and homogeneous. However, they are predominantly MWNTs with a considerably proportion of defects.

A study of the potential surplus value of $\alpha$-(Al$_{1-x}$Fe$_x$)$_2$O$_3$ foams, as opposed to powders, as catalytic materials for the CCVD synthesis of CNTs in H$_2$-CH$_4$ atmosphere, has demonstrated that the lower grain size and the higher specific
4 General Conclusions

surface area of the foams as compared to the powders do not lead to an easier reduction and thus to the formation of more Fe and/or Fe-carbide phases that constitute the potentially active particles for the nucleation and growth of CNTs. There is no gain in the CNT quantity, but HRTEM images revealed that the amount of SWNTs is considerably higher when the starting material is in the form of foam (60% SWNTs) as opposed to a powder with the same composition, which favours double-walled CNTs (only 5% SWNTs).

A thermal stability study of a selected CNT-Fe-Al₂O₃ nanocomposite powder has shown that Fe₃C decomposes at relatively low temperatures, while α-Fe and γ-Fe-C remain quite stable up to 670 °C and 850 °C, respectively. The oxidation of the Fe₃C and Fe particles results in the formation of hematite (α-Fe₂O₃). In-situ Mössbauer spectra acquired at high temperatures have shown that α-Fe₂O₃ forms as small particles (~25 nm).

Detailed information about the surface state of CNT-Fe-Al₂O₃ nanocomposite powders was obtained by comparative ILEEMS and transmission Mössbauer spectroscopic experiments. Using moderate reduction temperatures (800, 850 and 910°C) for the CNT synthesis resulted in nanocomposite powders for which the α-Fe and Fe₃C were not observed as surface species, while γ-Fe-C is present at the surface and in the bulk in the same proportion regardless of the reduction temperature. This finding suggests that the majority of the nanoparticles (Fe₃C and/or γ-Fe-C) that contribute to the formation of CNTs are located in the outer porosity of the material, as opposed to the top most surface layers.

As for the preparation of iron-substituted mullite powders [(Al,Fe)₆Si₂O₁₃], it was found that higher calcination temperatures resulted in a higher degree of crystallization and a lower specific surface area for the final product. Pure mullite could not be obtained and, as evidenced by the XRD patterns and by the Mössbauer spectra, an admixture with an α-(Al,Fe)₂O₃ phase could not be avoided, the contribution of the latter phase decreasing with the increase in the temperature of calcination. Using these powders as catalytic materials has for the first time permitted to prepare CNT-Fe-mullite nanocomposites by a reduction in H₂-CH₄ atmosphere. The Fe³⁺ ions present in both the mullite and corundum phases are reduced to form metallic particles that are detected as α-Fe, Fe₃C and γ-Fe-C. However, the major part of the Fe³⁺/mullite ions are only partially reduced to Fe²⁺ ions in a hercynite (FeAl₂O₄) phase.

The value of applying the Mössbauer spectroscopy technique for the study of CNT-Fe-oxide materials is that the identification and quantification of the various Fe-containing phases can be performed precisely (XRD is not able to quantify or clearly identify α-Fe, Fe₃C and γ-Fe-C when these phases are present as a mixture
between them and the ceramic matrix). Moreover, Mössbauer spectroscopy has the advantage of determining the oxidation state of iron. Thus, another important advantage of this technique is that the reduction rate of the starting solid solution(s) can be determined.

The combination of the still unique ILEEMS with conventional transmission Mössbauer spectroscopy has yielded a wealth of information concerning the understanding of the relationship between the starting catalytic material, the location of the reduced iron species (α-Fe, Fe\(_3\)C and γ-Fe-C) in the composite powders and the CNTs. Earlier hypotheses, into how these species may be connected to the formation of the CNTs, were refined: in particular, it was shown that γ-Fe-C particles are not obviously very small-sized nanometric particles and that the species active for the formation of CNTs are not always detected as Fe\(_3\)C.

At the end of this thesis work, it appears that many opportunities are still open for studies. Concerning the surface composition of CNT-Fe-oxide nanocomposites, Mössbauer spectroscopy (emission and transmission measurements) offers the possibility to investigate other CNT systems than the ones already presented in this work. The thermal stability study of the CNT-Fe-Al\(_2\)O\(_3\) nanocomposite powder, in particular using in situ transmission Mössbauer spectroscopy, opened the possibility for future studies dealing with other Fe-containing systems. Moreover, it would be very interesting to apply this technique during the CCVD in order to obtain more information of the true nature of the catalytically active species at the actual temperature where the CNTs nucleate and grow.
Part II

Papers
Paper I

Synthesis of $\gamma$-(Al$_{1-x}$Fe$_x$)$_2$O$_3$ solid solutions from oxinate precursors and formation of carbon nanotubes from the solid solutions using methane or ethylene as carbon source

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Synthesis of $\gamma$-(Al$_{1-x}$Fe$_x$)$_2$O$_3$ solid solutions from oxinate precursors and formation of carbon nanotubes from the solid solutions using methane or ethylene as carbon source

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This work reports for the first time the synthesis of $\gamma$-(Al$_{1-x}$Fe$_x$)$_2$O$_3$ solid solutions with a high specific surface area (200-250 m$^2$/g) by the decomposition of metal oxinate $[[\text{Al}_{1-x}\text{Fe}_x]_2\text{C_2H_4ON}_2]$ and investigated the potential of these materials as catalysts for the synthesis of carbon nanotubes by catalytic chemical vapor deposition using methane or ethylene as carbon source. The nanocomposite powders prepared by reduction in H$_2$-CH$_4$ contain carbon nanotubes (CNTs), which are mostly double-walled but also contain a fair amount of undesirable carbon nanofibers, hollow carbon particles, and metal particles covered by carbon layers. Moreover, abundant metallic particles are observed to cover the surfaces of the matrix grains. By contrast, the nanocomposite powders prepared by reduction in N$_2$-C$_2$H$_4$ are not fully reduced, and the CNTs are much more abundant and homogeneous. However, they are multiwalled CNTs with a significant proportion of defects. The powders were studied by several techniques including Mössbauer spectroscopy and electron microscopy.

I. INTRODUCTION

Fe-Al$_2$O$_3$ materials are of paramount importance as catalysts for the preparation of carbon nanotubes (CNTs) by catalytic chemical vapor deposition (CCVD) routes. It is generally and rationally conceived that the metal nanoparticles that are active for the catalytic decomposition of

the hydrocarbon are those located at the surface of the matrix grains. One method ensuring that the metal particles do not grow to sizes too large for the catalytic formation of CNTs involves the reduction in H$_2$-CH$_4$ gas atmosphere of alumina-hematite solid solutions, first producing nanometric Fe particles that are active for the decomposition of CH$_4$ thus subsequently producing carbon nanotubes-Fe-Al$_2$O$_3$ nanocomposite powders. A partial substitution of Al$^{3+}$ by Fe$^{2+}$ into the structure of the alumina has therefore been the subject of intensive research, in particular concerning the effects of the characteristics of the precursor material upon the synthesis of

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CNTs. Thus, attention was devoted to the influence of the iron content in the precursor material\(^2\) and to the different form and specific surface area of the solid solution.\(^3\)\(^4\) To maximize the quantity of CNTs, it is desirable that there are more surface nanoparticles. For a given iron content, this could be achieved by using a starting solid solution with a higher specific surface area (SSA) because this will result in a higher proportion of Fe\(^{3+}\) ions located at the surface rather than in the bulk of the oxide grains. Increasing the geometrical surface area by a grinding, which decreases the grain size of the starting powder, was not found\(^5\) to be useful, possibly because the much better packing of the ground powder hampers the supply of CH\(_2\) into the powder bed, which is detrimental to the growth of the CNTs. When using the high-SSA amorphous transition solid solutions prepared from the mixed-oxalate decomposition and calcination, it was found\(^\text{VI}\) that some undesirable carbon is entrapped within the Al\(_2\)O\(_3\) grains upon the crystallization into the corundum (α) form, which occurs during the reduction step performed at 900 or 1000 °C. Thus, the first part of this work is devoted to the preparation of high-SSA (200–230 m\(^2\)/g) γ-(Al\(_{1-x}\)Fe\(_x\))\(_2\)O\(_3\) solid solutions that are more stable and therefore resist the γ-α transformation. We use a novel route based on the decomposition of metal oxalates. Da Costa et al.\(^7\) have reported an alternative solvent-free method for the synthesis of metal-substituted Fe oxide. They have successfully prepared hematite (α-Fe\(_2\)O\(_3\)) with Al-for-Fe substitution from metal oxalates obtained by homogeneous precipitation. Other authors have prepared in a similar way Ni- and Zn-doped hematites.\(^8\) 8-Hydroxyquinoline (oxine) is a complexing agent that reacts with a variety of cations, producing compounds with general formula M(C\(_{5}\)H\(_4\)N\(_2\))\(_n\) (known as metal oxinate), where M is the cation and n is the valency of the cation, which can be equal to 2, 3, or 4\(^9\). According to Vogel\(^10\) Al and Fe cations precipitate in approximately the same pH range, i.e., 2.9 and 2.5, respectively. This aspect and the possibility of generating OH\(^-\) groups in situ by the decomposition of urea were examined by some authors, e.g., da Costa et al.\(^11\). In a second part of the study, the potential of these solid solutions as catalysts for the synthesis of CNTs by CCVD using methane or ethylene as the carbon source is investigated.

II. EXPERIMENTAL

A. Synthesis of the Al/Fe oxinates and γ-(Al\(_{1-x}\)Fe\(_x\))\(_2\)O\(_3\) oxide powders

Thirty grams of the 8-hydroxyquinoline (C\(_{5}\)H\(_4\)NO) were dissolved in 300 ml of acetic acid 3.5 M (20%). Subsequently, ammonium hydroxide was added dropwise until turbidity appeared; the solution was clarified by the addition of a minimal amount of acetic acid. To prepare 2 g of the (Al\(_{1-x}\)Fe\(_x\))\(_2\)O\(_3\) oxide, with x equal to 0.02, 0.05, 0.07 and 0.10, appropriate amounts of Al\(_2\)(SO\(_4\))\(_3\)-12H\(_2\)O and Fe\(_2\)(SO\(_4\))\(_3\)-12H\(_2\)O were dissolved in a mixture of 20 ml of HCl and 1 L of distilled water, using a 2-L flat-bottom boiling flask. Approximately 260 ml of the oxine solution and 70 g of urea were added into the flask, which was connected to a
condenser. This solution was boiled for 2 h. The products were filtered, washed several times with distilled water, and finally dried at 100 °C for 24 h. All Al-Fe oxinates [Fe(Al₁₋ₓFeₓ)(OH)ₓ(C₃H₃(NO))₃] are dark green.

Subsequent calcination in air of these products obtained the oxide solid solutions were performed at 800 °C, a temperature determined by the results of thermal analyses (see below). The oxinate precursors are henceforward named as OxAlFeX, and the fired samples are named as AFX [γ-(Al₁₋ₓFeₓ)ₓO₃], where X is the cationic % (wt.%) of Fe-or-Al substitution. Four different compositions of γ-(Al₁₋ₓFeₓ)ₓO₃ containing 2, 5, 7, and 10 cat % of Fe were prepared.

B. Synthesis of carbon nanotubes

CNT-containing nanocomposite powders were prepared by CVD method. The influence of the carbon source (CH₄ or C₃H₃) was investigated. Several batches of the solid-solution powders containing 2 and 5 cat % of iron (AF2 and AF5) were reduced in a H₂/CH₄ gas mixture (20 mol% CH₄). The heating and cooling rate to the desired final temperature (1000 °C) and back to room temperature, respectively, was 5 °C/min. No dwell time was applied at 1000 °C. The flowing gas was dried on P₂O₅, and its composition was controlled by mass-flow controllers. The total flow rate was 15 L/h. The so-obtained CNTs-Fe-Al₂O₃ nanocomposite powders are code named AFXRE, where "X" represents the iron content (cat.%) in the starting solid solution and "E" stands for ethylene.

C. Characterization

Thermogravimetric analysis (TGA) of the oxinates decomposition was performed using approximately 30 mg of each sample in a SETARAM TAG 24 module (simultaneous symmetrical thermal analyzer). The temperature ranged from 25 to 1000 °C, using a constant flow of synthetic air (25 ml/min) and applying a heating rate of 1 °C/min.

For identification of crystalline phases, x-ray diffraction (XRD) patterns were recorded in the range 10°–70° (2θ) using a Bruker D4 Endeavor diffractometer equipped with a Cu Kα radiation tube. Counts were registered every 0.02° (2θ). The background has been subtracted using the EVA software.

The SSA of the oxides was measured by the BET method (Micrometrics Flow Sorb II 2300) using nitrogen

TABLE I. Thermal behavior of the Al/Fe oxinates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T₁ (°C)</th>
<th>Weight loss 1 (%)</th>
<th>T₂ (°C)</th>
<th>Weight loss 2 (%)</th>
<th>Theoretical total weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OxAlFe2</td>
<td>350</td>
<td>23.2</td>
<td>480</td>
<td>63.6</td>
<td>86.8</td>
</tr>
<tr>
<td>OxAlFe5</td>
<td>356</td>
<td>25.6</td>
<td>433</td>
<td>62.2</td>
<td>87.8</td>
</tr>
<tr>
<td>OxAlFe7</td>
<td>354</td>
<td>27.8</td>
<td>422</td>
<td>59.3</td>
<td>88.5</td>
</tr>
<tr>
<td>OxAlFe10</td>
<td>352</td>
<td>30.2</td>
<td>408</td>
<td>57.4</td>
<td>87.6</td>
</tr>
</tbody>
</table>

*Temperature corresponding to minimum in the derivative of the TGA curves (DTG).

FIG. 3. XRD patterns of the γ-alumina-based solid solution: (a) AF2, (b) AF5, (c) AF7, and (d) AF10. The dash line indicates a gradual shift of the peak position at about 67° (2θ).

adsorption at liquid-nitrogen temperature. This instrument gives a SSA value from one point (i.e., one adsorbe pulse) and requires calibration. The reproducibility of the results was determined to be in the ±3% range.

Mössbauer spectra (MS) at 295 and 15 K were collected with a spectrometer operating at constant acceleration mode with triangular reference signals. 57Co(Rh) source was used. The spectrometer has been calibrated by collecting at 295 K the spectrum of a standard metallic iron foil. Isomer shifts are referenced with respect to α-Fe at room temperature.

The carbon content in the nanocomposite samples [C, (wt%)] was measured by the flash combustion method with an accuracy of ±2%.

Raman spectra were recorded using a LabRAM 800 Jobin-Yvon spectrometer (632.82 nm) and were averaged on three spectra.

Samples of the oxide and the nanocomposite powders were coated with platinum for observation by field-emission-gun SEM equipped with an in-lens electron detector (FE-SEM, JEOL JSM 6700F). The observations were performed under a tension of 5 kV, and the working distance was in the range 4-6 mm. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 1011 (100 kV) microscope. The preparation of samples for TEM imaging involved the dispersion of the powders in ethanol and subsequent deposition on a carbon grid. To study the distribution of the number of walls and the diameter of the CNTs, high-resolution TEM (HRTEM) has been performed using a JEOL JEM 2100F microscope operated at 200 kV. The magnification of the apparatus allowed to clearly resolve the walls of isolated CNTs, which were easily distinguished from other forms of carbon. The powders were slightly sonicated in ethanol to obtain a suitable dispersion without presumably provoking too much damage to the CNTs. A few drops of the suspension were subsequently deposited on a perforated carbon film attached to a copper grid. Only those CNTs that were contained within the holes of the carbon film were probed to avoid any interaction with the support.

III. RESULTS AND DISCUSSION

A. Al/Fe oxinates

Analysis of the XRD patterns (Fig. 1) of the Al/Fe oxinates show that all the main peaks coincide with those of e-Al-oxinate as reported by other researchers.9,10

Both the pure iron oxinate [Fe(C₅H₆ON)₃] and aluminium [Al(C₅H₆ON)₃] oxinate have been prepared in earlier years with the aim to study their thermal stability in air.1,12 These authors reported that [Fe(C₅H₆ON)₃] and [Al(C₅H₆ON)₃] are anhydrous, and that they are fairly stable below 335 and 375 °C, respectively, without weight loss of the sample in those ranges of temperatures. At higher temperatures in air, both iron and aluminium oxinates decompose to produce the respective oxides, i.e., Fe₂O₃ and Al₂O₃. The decomposition of the mixed Al/Fe oxinate can thus be described according to the global reaction (Eq. (1)):

\[
\text{[Al}_{1-x}\text{Fe}_x\text{(C}_5\text{H}_6\text{ON})_3\text{]}_2 \rightarrow 123/4 \text{O}_2\text{(g)} \rightarrow 1/2 \text{Al}_{1-x}\text{Fe}_x\text{O}_{3.5} + 27 \text{CO}_2\text{(g)} + 3/2 \text{N}_2\text{(g)} + 9 \text{H}_2\text{(g)}
\]

The TGA curves and the corresponding differential thermogravimetric (DTG) curves are reported in Fig. 2. No weight loss that could account for dehydration is observed between 25 and 280 °C. Two steps are observed at higher temperatures. The first one starts at 290 °C with a peak position practically unaffected by the iron content (T₁ = 356 ± 4 °C (Table I)). The second step, which slightly overlaps the first, takes place in a temperature range that is shifted to lower temperatures with increasing iron content (Table I). The peak position T₂ accordingly decreases from 480 °C (OxAlFe2) to 408 °C (OxAlFe10). This observation suggests that the iron ions were indeed coprecipitated with the aluminium ions. Beyond the second stage, the weight remains constant, giving confirmation that the decomposition is completed. For OxAlFe2, the experimental weight loss of the first step (Table I) was calculated to correspond to the loss of 9 mol of carbon for 1 mol of oxinate, producing 9 mol of CO₂ as proposed in reaction [Eq. (2)]. The second step was calculated (Table I) to correspond to the remainder of the decomposition reaction, according to reaction [Eq. (3)].
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**FIG. 4.** FEG-SEM images for sample AF5.

**FIG. 5.** Mössbauer spectra at 295 K of the $\gamma$-alumina-based solid solution (left). The probability of distribution is shown on the right side.

The experimental data (Table I) reveal that the proportion of the first step increases at the expense of that of the second one upon increasing the iron content. This

**TABLE II.** Hyperfine parameters at room temperature of $\gamma$-alumina solid solution with 2, 5, 7, and 10 cat. % Fe. The values of isomer shifts are with reference to metallic iron at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta E_{Q0}$ (mm/s)</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta E_{Q0,1}$ (mm/s)</th>
<th>$R_{A1}$ (%)</th>
<th>$\Delta E_{Q0,2}$ (mm/s)</th>
<th>$R_{A2}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF2</td>
<td>0.98</td>
<td>0.32</td>
<td>0.95</td>
<td>64</td>
<td>1.45</td>
<td>36</td>
</tr>
<tr>
<td>AF5</td>
<td>0.92</td>
<td>0.32</td>
<td>0.81</td>
<td>35</td>
<td>1.29</td>
<td>65</td>
</tr>
<tr>
<td>AF7</td>
<td>0.92</td>
<td>0.32</td>
<td>0.78</td>
<td>33</td>
<td>1.25</td>
<td>67</td>
</tr>
<tr>
<td>AF10</td>
<td>0.91</td>
<td>0.32</td>
<td>0.78</td>
<td>35</td>
<td>1.25</td>
<td>65</td>
</tr>
</tbody>
</table>

$\Delta E_{Q0,1}$; maximum probability quadrupole splittings; $\delta$; isomer shifts; $R_{A1}$; relative areas.

**FIG. 6.** XRD patterns of the nanocomposite powders prepared by reduction in H$_2$-CH$_4$, (●) $\gamma$-(Al$_x$Fe$_{1-x})$_3O$_3$; (●) Fe$_3$C; (△) graphite; and (△) α-Fe.
trend is in qualitative agreement with what is observed for the pure iron oxinate. However, this evolution should not be observed for the proposed reactions [Eqs. (2) and (3)]. Indeed, both weight losses should slightly diminish upon increasing the iron content. Some basic calculations reveal that the observed difference between the experimental and theoretical data is fairly well correlated with the iron content. This could mean that a part (possibly concerning the breaking of the C–O bond) of what is ascribed as occurring for the second step tends to be more and more occurring for the first one. This observation again supports the coprecipitation of the iron and aluminum ions. The total weight loss as determined experimentally from the TGA curves are, in average, approximately 1.2% lower than the theoretical values (Table I). This kind of deviation was observed by other authors dealing with oxinate reaction, and an explanation has not been found so far. Kumamaru et al. reported that the Al-oxinate is decomposed as opposed to vaporized in the presence of air, whereas it can be volatilized in absence of O₂. By contrast, TGA studies performed at 10°C/min in a flow of synthetic air and giving 100% weight loss, with increasing temperature prompted da Costa et al. to suggest that the Al-oxinate is volatile. However, Ribeiro et al. suggested that the relation between the vaporization and the quantity of solid residue
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<thead>
<tr>
<th>Sample</th>
<th>α-Fe</th>
<th>Fe&lt;sub&gt;3&lt;/sub&gt;C</th>
<th>γ-Fe-C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B&lt;sub&gt;hf&lt;/sub&gt;</td>
<td>δ</td>
<td>RA</td>
</tr>
<tr>
<td>AF2RM&lt;sup&gt;a&lt;/sup&gt;</td>
<td>33.0</td>
<td>0.00</td>
<td>22</td>
</tr>
<tr>
<td>AF5RM&lt;sup&gt;a&lt;/sup&gt;</td>
<td>33.0</td>
<td>-0.01</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>24.8</td>
<td>-0.05</td>
<td>30</td>
</tr>
<tr>
<td>AF2RM&lt;sup&gt;a&lt;/sup&gt;</td>
<td>34.5</td>
<td>0.12</td>
<td>25</td>
</tr>
<tr>
<td>AF5RM&lt;sup&gt;a&lt;/sup&gt;</td>
<td>34.5</td>
<td>0.12</td>
<td>13</td>
</tr>
</tbody>
</table>

<sup>a</sup>Hyperfine-field distribution from minimal 18.5 T to maximal 26.5 T for all MS.
<sup>b</sup>Also present are a weak sextet with B<sub>hf</sub> = 27.4 T, δ = 0.11 mm/s, and RA = 5%, and a weak ferric doublet with ΔE<sub>Q</sub> = 0.98* mm/s, δ = 0.32* mm/s, and RA = 6%.
<sup>c</sup>Also present is a weak sextet with B<sub>hf</sub> = 31.1 T, δ = 0.22* mm/s, and RA = 4%, a weak ferric doublet with ΔE<sub>Q</sub> = 0.98* mm/s, δ = 0.43* mm/s, and RA = 1%.

*Fixed parameter.
B<sub>hf</sub>, hyperfine field at the maximum of the distribution (T); 2ΔQ, quadrupole shift (mm/s); δ, isomer shift (mm/s); RA, relative area (%); T, temperature (K).

![FIG. 8. FE-SEM images of the CNTs-Fe-Al<sub>2</sub>O<sub>3</sub> nanocomposite powders prepared by reduction in H<sub>2</sub>-CH<sub>4</sub>: (a and b) AF2RM and (c and d) AF5RM.](image_url)

depends on the heating rate. As mentioned earlier in this section, the total weight loss was close to 87% for all of the present samples, including the pure aluminum oxinate (not discussed here), thus being in agreement with Ku mamuru et al.\textsuperscript{15} As an attempt to shed some light onto this question, additional TGA runs with different heating rates, and masses of samples were performed for the pure Al-oxinate and also for the sample with 2 cat.% Fe. A weight loss of 99% was observed for the run at 50 °C/min and using approximately 3 mg of sample, whereas 92% of loss was observed with a heating rate of 10 °C/min. This confirms the observation by Ribeiro et al.\textsuperscript{14} A complete study of these complex phenomena is beyond the scope of this article. A higher heating rate corresponds to a higher rate of input of thermal energy into the reactive specimen, favoring the occurrence of reactions and transformations in a shorter time span. Therefore, if there is a competition between a volatilization and a decomposition,
the instantaneous release of gas molecules by the latter reaction will change the partial pressures if the air flow is not high enough to instantaneously purge the atmosphere. The local conditions may then favor the vaporization until the proper atmosphere is restored. Hence, the inconsistencies described in the literature for the decomposition (temperature, observed weight loss, etc.) might be due to differences in the experimental conditions: heating rate, purge gas flow, mass of sample, and geometry of the sample pan.

B. γ-(Al<sub>1-x</sub>Fe<sub>x</sub>)O<sub>3</sub> oxide powders

Based on the TGA results, which showed that the decomposition is completed at a temperature below 600 °C, it has been decided to prepare the γ-(Al<sub>1-x</sub>Fe<sub>x</sub>)O<sub>3</sub> solid solutions by calcination of the powders at 800 °C for 1 h in a preheated furnace. The XRD patterns of the fired materials are shown in Fig. 3. The diffraction peaks are extremely broad, implying a nanosized average crystallite size (~3 nm). The centroids of the peaks are close to the peak positions of the XRD lines of standard γ-Al<sub>2</sub>O<sub>3</sub> (PDF card 29-1486). The eventual presence of hematite could not be detected. It seems that there is a gradual shift of all γ-alumina XRD peaks towards lower diffraction angles with increasing iron content, as shown by an inset dash line in Fig. 3. This behavior is expected when iron (Fe<sup>3+</sup>) ions replace aluminum (Al<sup>3+</sup>) ions in the lattice.

The SSA of the so-obtained γ-(Al<sub>1-x</sub>Fe<sub>x</sub>)O<sub>3</sub> oxides are in the range 200–230 m<sup>2</sup>/g with no apparent influence of the iron content. These values are a confirmation of the small particle size, possibly also reflecting the occurrence of pores. One can note that these values are significantly higher than those (approximately 30 m<sup>2</sup>/g) obtained for the η-(Al<sub>1-x</sub>Fe<sub>x</sub>)O<sub>3</sub> solid solutions prepared by calcination in air at 850 °C of the decomposition products of the corresponding mixed oxalates, and they are higher than the values (~128 m<sup>2</sup>/g) obtained after calcination at 550 °C of alumina precursors prepared by the combustion route.

FESEM images of a typical powder (AF5) show plate-like particles with a broad size distribution, the maximum being approximately 50 μm [Fig. 4(a)]. The surface of these plates is covered by grains approximately 2 μm in size [Figs. 4(b) and 4(c)], down to less than 50 nm in size [Fig. 4(d)]. The image at higher magnification [Fig. 4(d)] also reveals the nanometric crystallites at the surface of a plate-like particle.

MS were recorded at 295 K for all powders calcined at 800 °C. All spectra consist of a single Fe<sup>3+</sup> doublet (Fig. 5). All measurements have been done using a narrow velocity scale (~4 mm/s), implying a higher resolution. Note that no hematite was detected, in good agreement with the XRD results. The spectra were fitted with one quadrupole-splitting distribution (QSDs) using a linear correlation between the isomer shift and quadrupole splitting. The relevant Mössbauer parameters are listed in Table II. The evaluated QSD profiles are plotted on the right side of Fig. 5. The QSD profiles are consistently composed of two distinct maxima for the four involved samples. To quantify the profiles, superpositions of two Gaussian curves were fitted to the evaluated QSD profiles. Each of these Gaussians is characterized by the position of its maximum, ΔE<sub>QSD</sub> (i = 1, 2), as reported in Table II. γ-Al<sub>2</sub>O<sub>3</sub> is generally considered to be based on a defective spinel structure. The well-known, cubic spinel structure (usually denoted as AB<sub>2</sub>O<sub>4</sub>) has an fcc sublattice of oxygen ions, with A and B cations partially occupying the tetrahedral (T<sub>d</sub>) and octahedral (O<sub>6</sub>) sites, respectively. The total cation ratio for the spinel structures is 3:4, as opposed to 2:3 in the case of γ-Al<sub>2</sub>O<sub>3</sub> thus creating a defective spinel structure because of the vacancies imposed by such an arrangement to maintain the stoichiometry. The existence of tetrahedral and octahedral sites in the γ-alumina structure may explain the shape of the QSD profiles as
evaluated from the MS. But obviously, the presence of two maxima do not give any unambiguous information concerning the site occupancy, i.e., the iron and/or vacancy distribution. Conflicting conclusions are reported in the literature concerning the location and proportion of vacancies in the γ-alumina lattice. It has been mentioned that the vacancies are situated entirely in octahedral positions,\(^\text{18}\) entirely in tetrahedral positions,\(^\text{20}\) or in both sites. In the latter case, an approximate proportion of 64:36 for the tetrahedral to octahedral coordination was suggested.\(^\text{21}\) So far, there is no agreement about the vacancies occupation, although there is a broad consensus that the vacancies do not create a superstructure but appear to be randomly distributed within the unit cell. Because the γ-alumina (spinel structure) has octahedral and tetrahedral lattice sites, it is likely that the Fe\(^{3+}\) cations are distributed among these two environments. The isomer-shift data presented in Table II support this suggestion. For γ-Fe\(_2\)O\(_3\) (maghemite, also possessing a defective spinel structure), external-field MS have shown that A-site Fe\(^{3+}\) has a δ value of −0.25 mm/s (298 K), whereas for B-site Fe\(^{3+}\) a value of −0.35 mm/s was found.\(^\text{22}\) The presently observed average δ values for the γ-alumina phase are in between these maghemite results. More specific details about the Fe\(^{3+}\)-cation distribution in the respective spinel structure cannot be concluded from the present MS.

C. Synthesis of CNTs

1. CNT nanocomposite powders prepared using methane as carbon source

Because the γ-α transition temperature decreases with the increase in the iron content in the solid solution and
In general, three components were found to be required to obtain adequate fits for the MS at 295 and 15 K (Fig. 7, left) of the nanocomposite powders: (i) an outer sextet due to \( \alpha \)-Fe; (ii) an inner asymmetrical six-line pattern that can be ascribed to ferromagnetic cementite; and (iii) a singlet.

For sample AF2RM, an additional, but weak (\(-5\%\) of total absorption area) and rather ill-defined sextet with hyperfine parameters \( \delta = 0.11 \text{ mm/s} \) and \( B_{dd} = 27.4 \text{ T} \) at 295 K, clearly appears in the MS [shaded in gray in Fig. 7(a)] and can be ascribed to an iron carbide phase (Table III). Its hyperfine parameters are indeed in good agreement with those reported by Bauer-Grosse et al. for an amorphous \( \text{Fe}_{1-x} \text{C} \) alloy with \( y = 0.19 \) (\( \delta = 0.13 \text{ mm/s} \) and \( B_{dd} = 27.4 \text{ T} \) at 295 K). In addition, for AF25RM, a weak Fe\(^{56}\) doublet (\(-6\%\) of the total area) is present in the MS collected at 295 K [shaded in light gray in Fig. 7(a)]. An adequate fit was obtained by fixing this doublet's hyperfine parameters at the values reported in Sec. III. B for \( \gamma \)-alumina solid solution (\( \Delta E_{Q} = 0.98 \text{ mm/s} \) and \( \delta = 0.32 \text{ mm/s} \)). Therefore, this doublet can be attributed to a minor amount of Fe\(^{56}\) that has remained within the precursor grains after the reduction treatment.

To resolve the sextet of the \( \alpha \)-Fe, single Lorentzian line shapes were used. Its quadrupole shift was forced to be zero. The Mössbauer parameters of \( \alpha \)-Fe are those of bulk iron, and no (super)paramagnetic effect is observed. Therefore, particle-size effects are not observed in the obtained Mössbauer parameters. However, particles of small size can be expected. Bodker and Morup have shown that ultrafine metallic iron particles prepared on a carbon support can exhibit bulk Mössbauer parameters down to a diameter of 2 nm. The present \( \alpha \)-iron particles can be compared to the nanoparticles observed in the various CNT-systems such as CNTs-Fe-MgO, CNTs-Fe-MgAl\(_2\)O\(_4\), and CNTs-Fe-Al\(_2\)O\(_3\).

Cementite (Fe\(_3\)C) has two inequivalent crystallographic Fe-sites, which are magnetically and electronically similar. For the spectra presented in Fig. 7(left), an asymmetry in the cementite six-line patterns is obvious, notably in the MS collected at 15 K. In particular, the first line is deeper and narrower than the sixth line. This observation is in line with the results obtained by Bi et al., who have shown that the differences between the Mössbauer parameters of the two iron sites of cementite increase with decreasing temperature. Thus, the most reliable fits for the six-line subpatterns of cementite were obtained using hyperfine-field distributions with linear correlations between isomer shift and hyperfine field and between quadrupole shift and hyperfine field. Clearly, two well resolved maxima appear in the calculated distribution profiles (Fig. 7, right), and these beyond any doubt reflect the existence of above-mentioned distinct Fe sites. The Mössbauer parameters
corresponding to these two maxima are indeed in excellent agreement with results reported by Bi et al.\textsuperscript{19} for nanoparticles of Fe\textsubscript{5}C measured at room temperature and 12 K.

The total absorption area of the singlet remains, within the experimental error, the same for both at 295 and 15 K, implying no relation with the other phases observed in the MS. A considerable broadening of the singlet is observed at 15 K. For this temperature, a low hyperfine-field sextet was used instead of a singlet to fit the spectra, yielding a more adequate reproduction of the central part of the spectra. This finding implies that the corresponding Fe phase undergoes a magnetic transition at "ultra" low temperature. According to Weiss\textsuperscript{33} and Coquay et al.\textsuperscript{26} the isomer shift value of the singlet at 295 K and its broadening at temperatures below 80 K are typical of γ-Fe, which indeed is known to order antiferromagnetically at low temperatures.\textsuperscript{32,33} The existence of a stable antiferromagnetic γ-Fe phase at low temperature can be explained by the presence of carbon atoms in the lattice of the γ-Fe structure and by the small size of the particles as reported by Coquay et al.\textsuperscript{26} Indeed, in γ-Fe-C (austenite) the carbon atoms are in the interstitial sites of the fcc γ-structure and, as such, can stabilize the structure at room temperature.\textsuperscript{34,35} Kachi et al.\textsuperscript{26} reported that the transformation of γ-Fe to α-Fe, which takes place at 910°C for bulk iron, is hindered in γ-Fe-Ni (with low Ni content) leading to an antiferromagnetic phase at low temperature. This feature seems to be related to the behavior of the small γ-Fe-C particles present in the nanocomposite powders, although in the case of γ-Fe-Ni the Ni atoms are substitutional.

The carbon content (C\textsubscript{n}) in the composite AF2RM powder is close to 5.7 wt%, and it is more than double for AF5RM (14.6 wt%). Obviously, the increase of the C\textsubscript{n} value is a consequence of the increase of the iron content.
TABLE IV. Mössbauer parameters of the nanocomposite powders prepared by reduction in Nz: C2H4 (samples BE) measured at 295 and 15 K. The values of isomer shifts are with reference to metallic iron at room temperature.

<table>
<thead>
<tr>
<th>Samples</th>
<th>B02</th>
<th>2ε0</th>
<th>8</th>
<th>RA</th>
<th>ΔE2</th>
<th>B</th>
<th>RA</th>
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<tbody>
<tr>
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<td>20.1</td>
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<td>0.17</td>
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<td>0.98</td>
<td>0.32</td>
<td>8</td>
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<tr>
<td>AF58E</td>
<td>19.9</td>
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<td>0.98</td>
<td>0.32</td>
<td>9</td>
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<tr>
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<td>20.5</td>
<td>0.02</td>
<td>0.18</td>
<td>89</td>
<td>0.98</td>
<td>0.32</td>
<td>7</td>
</tr>
<tr>
<td>AF98E</td>
<td>19.9</td>
<td>0.01</td>
<td>0.18</td>
<td>89</td>
<td>0.98</td>
<td>0.32</td>
<td>7</td>
</tr>
<tr>
<td>AF26E</td>
<td>26.3</td>
<td>0.02</td>
<td>0.19</td>
<td>89</td>
<td>0.98</td>
<td>0.32</td>
<td>7</td>
</tr>
<tr>
<td>AF29E</td>
<td>25.7</td>
<td>0.03</td>
<td>0.32</td>
<td>95</td>
<td>1.03</td>
<td>0.44</td>
<td>4</td>
</tr>
</tbody>
</table>

- Fixed parameter.
- a,b A weak singlet due to γ-Fe-C is present. The hyperfine parameters for this phase have been fixed according to values reported by Coquy et al.
- b, c, d, e, f, g, h: hyperefine field (T), 2ε0: quadrupole shift (mm/s), ΔE2: quadrupole splitting (mm/s), b: isomer shift (mm/s), RA: relative area (%), T: temperature (K).

in the starting solid solution, in line with earlier studies, because more catalytic particles will be available for the decomposition of methane. The high-frequency range (1100–1800 cm⁻¹) of the Raman spectra (data not shown) shows the D band (-1328 cm⁻¹) and the G band (-1580 cm⁻¹) with a shoulder at higher frequency (-1650 cm⁻¹). This shoulder is typical of defective graphite-like materials and is usually observed for MWNTs. The shoulder is more intense for AF5RM than for AF2RM. Accordingly, the ratio between the intensities of the D band and the G band, ID/IG, is higher for AF5RM than for AF2RM (132 and 53%, respectively). An increasing ID/IG value corresponds to a higher proportion of sp²-like carbon, which is generally attributed to the presence of more structural defects. The presence of radial-breathing-modes (RBM) peaks in the low-frequency range (100–300 cm⁻¹) of the spectrum, the frequencies of which are inversely proportional to the CNT diameters, is usually the sign of the presence of small-diameter CNTs, such as single- and double-walled CNTs (SWNTs and DWNTs, respectively). Only weak RBM peaks are observed for the present specimens. Note however that the Raman process is influenced by optical resonance, and it is thus impossible to detect all of the present CNTs using only one wavelength. Moreover, the peak intensities do not reflect the real amount of individual CNT because of the resonance effect, which amplifies the Raman signal from certain CNT.

The FEG-SEM images of AF2RM reveal the presence of long, flexible filaments, with a smooth and regular surface, on the surface of the oxide grains [Fig. 8(a)] and bridging several grains [Fig. 8(b)]. All filaments have a diameter smaller than 30 nm and a length of the order of some tens of micrometers. From the results of previous studies, it is known that such filaments are isolated CNTs and/or CNT bundles. Spherical particles, which may be α-Fe, γ-Fe, and/or Fe-C, are observed at the matrix surface [some of which are labeled P in Fig. 8(c)]. The diameter of these particles ranges between 5 and 20 nm. Most of these particles do not appear to be connected to a CNT, indicating that they have been inactive for the formation of CNT in the present experimental conditions. Moreover, the presence of thick, short carbon nanofibers [labeled CNF on Fig. 8(c)] is observed. Such CNF are similar to some species commonly observed in works on filamentous carbon. The formation mechanisms are different from those thought to occur in the case of CNTs. The FEG-SEM images of AF5RM are similar, but more CNF are observed. Some groups of large carbon particles (up to 300 nm in diameter) [labeled CP on Fig. 8(d)] are observed. How they were formed is unclear.

Typical TEM images collected for sample AF5RM are shown in Fig. 9. Bundles of CNTs, CNF, and metallic particles are observed. Typical HRTEM images for the various species are shown in Fig. 10. DWNTs with a diameter either higher or lower than 5 nm are shown in Figs. 10(a) and 10(b) and Figs. 10(c) and 10(d), respectively. A CNT with five walls and a particle within a shell formed of several graphene layers are shown in Fig. 10(e). Figure 10(f) reveals the defects present in some large diameter CNTs. Bamboo-like CNFs, empty or partly filled with a metal particle, are shown in Figs. 10(g) and 10(h). Particles within shells formed of many graphene layers, approximately 10 nm in diameter, are shown in Fig. 10(i). Large, hollow carbon particles that appear to be poorly organized are shown in Fig. 10(j). Figure 11 presents histograms of the (a) particle size, (b) number of walls, and (c) diameter distribution of the CNTs, which were obtained by measuring nanoparticles and CNTs on similar HRTEM images for sample AF5RM. The particle size falls in the range 5–20 nm, revealing an average diameter of ~10 nm [Fig. 11(a)]. Theoretical and experimental results have shown that CNTs are produced by catalytic particles below 3–6 nm in diameter, whereas particles in the size range approximately 6–10 nm are encapsulated by carbon layers, and the larger ones produce nanofibers, short filaments, and bamboo. Therefore, the large majority of metallic particles observed in the present samples are those
FIG. 13. SEM images of the CNT-Fe-Al \(_2\)O \(_3\) nanocomposite powders prepared by reduction in \(N\_2-C\_3H\_8\): (a) AF2RE, (b) AF5RE, (c) AF7RE, and (d) AF10RE.

FIG. 14. HRTEM images for sample AF5RE showing different forms of carbon observed in the nanocomposite powder.

Actually expected to be too large to produce CNTs. The distribution of the number of walls [Fig. 11(b)] shows that most of CNTs are DWNTs and triple-walled CNTs (3WNTs), their total abundance being 78%. The width of the diameter distributions for all measured CNTs exhibit broad ranges, the averages being ~3.3 and ~4.7 nm for the inner and outer diameter, respectively [Fig. 11(c)]. Combining the SEM and TEM results for both AF2RM and AF5RM samples, it can be inferred that a substantial amount of large metallic particles at the surface of the matrix grains have been formed during the reduction and thus have not been active for CNT formation, but rather for the formation of undesirable carbon species. Whatever the iron content used in the present study, the
reduction of the $\text{Fe}^{3+}$ ions of the $\gamma-(\text{Al}_2\text{Fe}_3)\text{O}_5$ solid solutions, producing iron nanoparticles, occurs at a temperature that is too low for the catalytic decomposition of methane to take place at the surface of the so-obtained nanoparticles. Thus, most nanoparticles are able to grow, the more so for a higher iron content, because there is no (or too little) solid carbon deposited at their surface to block the process. When the catalytic decomposition of methane does take place at the surface of the nanoparticles, the smaller ones indeed produce a CNT, but the larger ones do not, rather they produce a CNF or become fully covered by graphene layers. Thus, the use of a carbon source, ethylene, that is able to decompose at a lower temperature than methane will be investigated in the next section.

2. CNT nanocomposite powders prepared using ethylene as carbon source

In the following part of the study, we attempted to perform the reduction at a lower temperature (800 °C), using $\text{N}_2$-$\text{C}_2\text{H}_4$ atmosphere. As mentioned above, ethylene decomposes at a lower temperature than methane, and, moreover, a lower reduction rate of the Fe$^{3+}$ ions would produce, for a given time, a lower amount of metallic phase, which would also favor the formation of smaller Fe particles. The XRD patterns (data not shown) of the AF2RE, AF5RE, AF7RE, and AF10RE nanocomposite powders showed essentially the diffraction peaks due to $\gamma$-alumina. The presence of Fe and Fe$_2$C is not confirmed unequivocally due to the overlapping with the diffraction lines of the $\gamma$-alumina. Graphite and/or MWNTs may be present as well.

Three components were found to be necessary to fit the MS: (i) an asymmetrical sextet ascribed to Fe$_2$C; (ii) a Fe$^{3+}$ doublet; and (iii) a singlet due to $\gamma$-Fe-C. It is interesting to note that no $\alpha$-Fe was found, probably because the reduction atmosphere contains no $\text{H}_2$. Examples of the MS at 295 and 15 K are shown in Fig. 12, for samples AF5RE and AF10RE, respectively. The hyperfine parameters for all of the samples are listed in Table IV. The Fe$^{3+}$ doublet was assumed to be due to the Fe$^{3+}$ ions present in the structure of the unreacted $\gamma$-alumina. Some restrictions had to be imposed for the interaction procedure to reach convergence with reasonable parameter values. These restrictions are specified in the footnotes to Table IV. The single line present in the spectra was attributed to $\gamma$-Fe-C. The RA of the singlet is merely less than 5% at room temperature. To obtain a better fit of the spectra, the hyperfine parameters for $\gamma$-Fe-C component had to be fixed in values reported in Sec. III, C, 1. Due to the small contribution of the $\gamma$-Fe-C and Fe$^{3+}$ components, the Mössbauer parameters are extremely ill-defined, and no further attention has been paid to them.

The carbon content increases upon the increase of the iron content in the solid solution (33.5, 39.8, 48.5, and 53.0 wt% for AF2RE, AF5RE, AF7RE, and AF10RE, respectively). It is interesting to note that these values are much higher than those obtained when using methane (5.7 and 14.6 wt% for AF2RM and AF5RM, respectively). A similar result has been obtained when using other catalysts.

FEG-SEM images (Fig. 13) revealed that the powders prepared by reduction in $\text{N}_2$-$\text{C}_2\text{H}_4$ are different and much more homogeneous than those prepared by reduction in $\text{H}_2$-$\text{CH}_4$. Indeed, the matrix grains are covered by a web-like network of carbon filaments not larger than 60 nm in diameter and several tens of micrometers long. The quantity of filaments increases with the increase in the content of iron. HRTEM images (Fig. 14) revealed that the filaments, most of which have a diameter lower than 15 nm, are MWNTs with many defects in the walls structure [Figs. 14(a) and 14(b)]. Disordered carbon is observed at the surface, but most of it is formed during the observation because the CNTs, notably the thinner [Fig. 14(c)], are damaged by the electron beam. Some ribbons [Figs. 14(d) and 14(e)], helix-shaped CNTs [Figs. 14(c) and 14(f)], and carbon particles, sometimes arranged as bamboo-nanofibers [Fig. 14(g)], are observed too. These observations are in good agreement with the results reported by other authors using ethylene as the carbon source and different catalytic materials.

Raman spectra (data not shown) show the D and G bands but no RBM. The $I_{2D}/I_{2G}$ values calculated from the spectra are high (approximately 135%) for all powders. This is slightly higher than the values reported by Qian et al., but it is in good agreement with the present electron microscopy observations. Interestingly, McCalpin et al. showed, using a different catalytic material, that the formation of the various carbon forms (platelet nanofibers, herringbone nanofibers, MWNTs, and encapsulated metal particles) strongly depends on the temperature and gas mixture composition. The present reduction conditions applied to the $\gamma-(\text{Al}_2\text{Fe}_3)\text{O}_5$ solid solutions already produce mostly MWNTs. Fine-tuning them could yield higher-quality MWNTs.

IV. CONCLUSIONS

This work reported for the first time the synthesis of $\gamma-(\text{Al}_2\text{Fe}_3)\text{O}_5$ solid solutions with a high specific surface area (200-230 m$^2$/g) by the decomposition of metal oxinate [(Al$_{13}$Fe$_3$C$_6$H$_{28}$O$_{34}$)$_3$] at 800 °C and the preparation of CNT nanocomposite powders from these solid solutions using methane or ethylene as the carbon source. The Mössbauer spectroscopy results showed that for the present $\gamma$-alumina (spinel structure) samples, the Fe$^{3+}$ cations are distributed among the octahedral and tetrahedral lattice sites. More specific results of the Fe$^{3+}$ proportions on the two respective environments could
not be inferred by the presented Mössbauer results because its isomer shift values are similar. The potential of these solid solutions as catalysts for the synthesis of carbon nanotubes by CCVD is then investigated. As evidenced by the Mössbauer spectroscopy results, 1000 °C is a high enough temperature to reduce all Fe⁺⁺ ions substituting the γ-(Al₁₋ₓFeₓ)₂O₃-based solid solution to metallic state in the H₂–CH₄ atmosphere with 20 mol% CH₄, with the exception of the sample with the lower iron content (x = 0.02). The proportions of γ-Fe₂C remain more or less constant, whereas the proportions for the other components (α-Fe and Fe₃C) vary from one powder to another. The nanocomposite powders prepared by reduction in H₂–CH₄ at 1000 °C contain CNTs which are mostly double-walled but also a fair amount of undesirable carbon nanofibers, hollow carbon particles, and metal particles covered by carbon layers. Moreover, abundant metallic particles are observed to cover the surface of the matrix grains. The reduction of the Fe⁺⁺ ions of the γ-(Al₁₋ₓFeₓ)₂O₃ solid solutions occurs at a temperature that is too low for the catalytic decomposition of methane to take place at the surface of the so-obtained iron nanoparticles. So the amount of solid carbon is insufficient to block the growth of the iron nanoparticles and to induce the nucleation of CNTs. By contrast, the nanocomposite powders prepared by reduction in N₂–C₂H₄ at 800 °C are not fully reduced, and the CNTs are much more abundant and homogeneous. However, they are mostly MWNTs with a significant proportion of defects. Work is in progress to fine-tune the N₂–C₂H₄ reduction conditions to increase the selectivity towards higher-quality MWNTs.

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Presence of metallic Fe nanoclusters in \( \alpha-(\text{Al,Fe})_2\text{O}_3 \) solid solutions


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Presence of Metallic Fe Nanoclusters in α-(Al_1-xFe_x)O_3 Solid Solutions

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Powders of γ-(Al₁₋ₓFeₓ)O₃ solid solutions prepared by the calcination in air of the corresponding γ-(Al₁₋ₓFeₓ)O₃ powders were studied by several techniques including X-ray diffraction, field-emission-gas-scanning electron microscopy, transmission Mössbauer spectroscopy, integral low-energy electron Mössbauer spectroscopy (ILEEMS), and Fe K-edge X-ray absorption near-edge structure (XANES) measurements. The asymmetry of the characteristic Mössbauer doublet representing Fe³⁺ ions substituting for Al³⁺ ions in the corundum lattice of α-(Al₁₋ₓFeₓ)O₃ solid solutions was resolved and explained for the first time by using two additional subspectra, i.e., a broad second doublet characteristic of a very distorted octahedral site for Fe³⁺ and a singlet attributable to α-Fe, suggesting the presence of metallic iron nanoclusters consisting of only a few number of atoms within the solid solution grains. ILEEMS studies showed that the Fe nanoclusters are evenly distributed among the surface layers and the cores of the grains. Fe K-edge XANES measurements further confirmed the occurrence of metallic iron. The proportion of Fe nanoclusters increases when the total iron content is decreased, as does the proportion of distorted octahedral site, suggesting that they are located around the iron nanoclusters. The formation of the metallic Fe nanoclusters in the α-(Al₁₋ₓFeₓ)O₃ grains is thought to be a consequence of the γ → α phase transition which implies structural rearrangement on both the cationic and anionic sublattices.

Introduction

Alumina, α-Al₂O₃, possess the corundum structure which is based on a hexagonal close-packed (hcp) array of oxygen anions, where 3/4 of octahedral (O₆) interstices are occupied by aluminum cations in a regular way.1 α-(Al₁₋ₓFeₓ)O₃ solid solutions have been studied for decades usually in order to determine the solubility limit of hematite (α-Fe₂O₃) into α-Al₂O₃2-10 but also as precursor materials for the formation of Fe-Al-O₃-x11-12 and carbon nanotube-Fe-Al-O₃-x13-14 nanocomposite powders by reduction in H₂ and H₂-CH₄, respectively. Several values have been reported for the solubility limit, in the range of 5-15 mol % (corresponding to 15-9 % of Fe³⁺ ions substituting for Al³⁺ ions in the corundum lattice of alumina). It appears that this strongly depends on the synthesis route. In particular, several methods permit the formation of solid solutions between the metastable sesquioxides of iron (γ-Fe₂O₃) and alumina (γ-Al₂O₃, δ-Al₂O₃, η-Al₂O₃, and θ-Al₂O₃). The structure of all these metastable oxides is related to that of spinel (MgAl₂O₄), owing to the ability of both Fe³⁺ and Al³⁺ ions to occupy tetrahedral (T₁) sites. The stoichiometry can be formally described by the formula Fe(x)Mg(2-x)Al₂O₄ whereas with the brackets indicating those species occupying the O₆ sites. It is well-known15-18 that an appropriate heat-treatment of such metastable γ-(Al₁₋ₓFeₓ)O₃ solid solutions can produce α-solid solutions without any phase partitioning into an alumina-rich corundum phase (αₐ) and a hematite-rich corundum phase (αᵦ).

Mössbauer spectroscopy was used as a unique characterization tool in the course of these investigations. Interestingly, several studies where the solid solutions were prepared using chloride2-5 sol-gel6,7 oxalate8,9 and combustion10 reported that the characteristic doublet representing Fe³⁺ ions substituting for Al³⁺ ions in the corundum lattice more or less clearly exhibited a significant asymmetry, which was never satisfactorily accounted for. Several authors9,10 applied an extended velocity scale, making the asymmetry less enhanced and consequently thought to be insignificant. The explanations proposed by Brown et al.8 and Cordier et al.11 will be discussed later in the text.

With the aim to shed some light into this matter, α-(Al₁₋ₓFeₓ)O₃ powders were prepared by an oxinate route different from all those used earlier. The present paper reports a major interdisciplinary research project concerning some remarkable features, believed to be related to the γ → α transition, involving for the first time the presence of metallic Fe nanoclusters within α-(Al₁₋ₓFeₓ)O₃ grains.

Experimental Section

γ-(Al₁₋ₓFeₓ)O₃ powders (containing 2, 5, 7, and 10 cat % Fe) with a high specific surface area (over 200 m²/g) were
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prepared from the decomposition of the mixed oxalates. The details of the preparation of the γ-(Al1-xFe2O3) powders will be reported elsewhere. To determine the γ → α transition temperatures, differential thermal analyses (DTA) were carried out (Du Pont SCDT 2900) on small samples of each powder. The DTA curves were recorded in the range 25–1300 °C using a flow of synthetic air (100 mL/min) and a heating rate of 10 °C/min. On the basis of the DTA results, the γ-(Al1-xFe2O3) powders were appropriately heat-treated in air in order to obtain the respective α-phases. The resulting α-(Al1-xFe2O3) powders were code-named as a-APY in which γ stands for the Fe content expressed as cat %. Powder X-ray diffraction (XRD) patterns were recorded in the range 20–70° (2θ) using a Seifert 3003 TTR diffractometer equipped with a Cu Kα radiation tube. The cell parameters were calculated by the Rietveld method using the Fullprof software.13 The specific surface area of the a-APY powders was measured by the Brunauer–Emmett–Teller (BET) method (Micrometrics Flow Sorb II 2300) using nitrogen adsorption at liquid nitrogen temperature. This instrument gives a value from one adsorbate pressure and requires calibration. The reproducibility of the results is in the 3% range. The powders were further examined by field-emission-gun SEM (FEG-SEM, JEOL JSM 6700F). Mössbauer spectra (MS) at 295 K and 4.2 K were collected with a spectrometer operating at constant acceleration mode with triangular reference signal. 57Co(Rh) source was used, but isomer shifts quoted hereafter are referenced with respect to α-Fe at 295 K. The absorbers had a thickness of at most approximately 7 mg of Fe per cm2. Velocity calibration was achieved by recording spectra of an α-Fe foil or a standard thin α-Fe2O3 absorber at room temperature. For the latter the inner line width was typically 0.27 mm/s. A selected sample was studied by integral low-energy electron Mössbauer spectroscopy (ILEEMS). ILEEMS is a variant of conventional transmission Mössbauer spectroscopy in which the resonant low-energy (~10 eV) electrons are counted.14 These electrons are produced by after effects in the decay process of the excited probe Mössbauer nuclei in the absorber following resonant absorption of incident γ-quanta. Combined with transmission Mössbauer spectroscopy, the results of ILEEMS yield semiquantitative information about the chemical state of a thin surface layer (~10 nm) of the material from which the majority of the detected low-energy electrons originate.

Fe K-edge XANES spectra were recorded at room temperature at the European Synchrotron Radiation Facility on the undulator beamline ID263:6 operating at 6 GeV and 200 mA in 2θ/2θ filling mode. A fixed-exit Si (311) double-crystal monochromator was used. The energy was calibrated by defining the first derivative peak of a metallic Fe reference foil to be 7112.0 eV. Two Si mirrors were used for the harmonics rejection of the incident X-ray beam. XANES data were recorded in quick-scan mode by simultaneously scanning the monochromator angle and the undulator gap with a typical energy step of 0.2 eV in the pre-edge region. The spectra were acquired in fluorescence mode, using a Si photodiode. The incident flux was monitored by detecting the X-ray scattering from a thin Kapton foil in the incident beam path. The sample was positioned at 45° with respect to the beam. Experimental X-ray absorption near-edge structure (XANES) spectra were reduced by background subtraction with a linear function and then normalized for atomic absorption on the average absorption coefficient of the spectral region from 7150 to 7250 eV. Pre-edge peak analysis was carried out following the procedure reported in Wilke et al.17 and Giulii et al.8 The pre-edge peak was fitted by a sum of pseudo-Voigt functions.

Results and Discussion

The DTA curves of all four powders exhibit an exothermic peak at a temperature that slightly decreases with increasing Fe content from 1097 °C for 2 cat % to 1069 °C for 10 cat % (Figure 1). This peak is assigned to the γ → α phase transition, and the observed correlation with Fe substitution is in agreement with earlier results.4,9,10 However, the γ-(Al1-xFe2O3) samples with 7 and 10 cat % Fe exhibit a second exothermic peak at ~1234 °C, which is, according to the XRD patterns (being presented hereafter), attributable to phase partitioning into an alumina-rich corundum phase (αH) and a hematite-rich corundum phase (αO).

On the basis of the above DTA results, the γ-(Al1-xFe2O3) powders were calcined at 1120 °C (2 and 5 cat % Fe) or 1100 °C (7 and 10 cat % Fe), in order to obtain the respective α-phases. The samples were heated up to 600 °C at a rate of 300 °C/h and then further heated at a rate of 900 °C/h up to the desired temperatures of 1120 or 1100 °C, respectively. A dwell time at these temperatures of 30 min was applied, and subsequently the products were allowed to cool down to room temperature at furnace rate, thus finally yielding the various a-APY samples.

The XRD patterns of the a-APY samples (Figure 2) show peaks characteristic of well-crystallized corundum solid solution. For a-APF10, however, several weak additional lines corresponding to hematite (α-Fe2O3) are observed. This indeed implies that for this composition the crystallization of the solid solution into the α phase was followed by some degree of phase partitioning. This result is in agreement with the DTA result as mentioned above. This finding further infers that the solubility limit of hematite into the α-Al2O3 structure for the present synthesis route is below 10 mol %. The hexagonal unit-cell parameters a and c of the a-APY samples as obtained from the XRD data were plotted (Figure 3) as a function of the iron content after having corrected the cat % for the fraction of Fe3+ cations present in the hematite phase, the latter being determined from the MS (see hereafter). Both a and c increase with increasing iron content, implying that the Fe3+ cations, which possess a larger ionic radius as compared to Al3+, are at substitutional sites in the corundum structure. The experimental
Figure 2. XRD patterns of the powders prepared by calcination in air of the corresponding \( \gamma-(\text{Al}_2\text{Fe}_3\text{O}_10) \) solid solutions. \( H \) = hematite; \( a \) = alumina.

Figure 3. (a) Cell parameter \( a \) and (b) cell parameter \( c \), as obtained from the XRD patterns. The black squares correspond to the experimental \( a \) and \( c \) cell parameters. The errors for the experimental points are smaller than their size (black squares). The solid line is a linear fit through the experimental points, and the dashed line represents the Végar's law.

\( a \) and \( c \) data are compared with the values predicted by Végar's law (dashed straight lines in Figure 3), using for the latter the lattice parameters of \( \alpha-\text{Al}_2\text{O}_3 \) as reported on the PDF card (83–2080) and those of a \( \alpha-\text{Fe}_2\text{O}_3 \) powder prepared by the oxinate decomposition route as given by da Costa et al.\(^{15}\) It is clear that both unit cell parameters for the present aAFY samples deviate from the corresponding Végar values. These deviations may be due to the presence of strain in the lattice which is eventually removed by the partial phase partitioning in those samples with higher Fe contents. Another possible explanation is the formation of metallic iron clusters, which will be presented and discussed in the following MS section.

Figure 4. FEG-SEM images of the aAF5 powder.

FEG-SEM images of the powders reveal that they are made up of 2–5 \( \mu \text{m} \) grains assembled into tabular-like aggregates (parts a and b of Figure 4). However, the observation of smaller entities and of side-views of the tabular-grains reveals the so-called vermicular microstructure with much looser aggregates made up of 0.2–0.5 \( \mu \text{m} \) primary grains or crystallites (Figure 4c). The BET specific surface area of the aAFY powders was found to be about 5 \( \text{m}^2/\text{g} \), much lower than for the parent \( \gamma-(\text{Al}_2\text{Fe}_2\text{O}_5) \) powders (over 200 \( \text{m}^2/\text{g} \)). This results from the strong structural rearrangement occurring on both the cationic and anionic sublattices that has taken place during the transformation process and from a high degree of sintering.

MS (Figure 5) were recorded at 295 K for the four aAFY powders described above. In view of the results thereof, two additional compositions were prepared in the same manner and
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Figure 5. Mössbauer spectra of the α-(AlFe)₃O₇ samples measured at room temperature and the respective spectral fitting residuals. The doublet D2 with large quadrupole splitting is shaded in olive while the singlet Sg due to Fe clusters is shaded in red and the doublet D1 with smaller quadrupole splitting is shaded in blue. The residuals are shown above each spectrum.

characterized by their Mössbauer spectra. These two additional samples contained 0.5 and 1 cat % Fe (αAF05 and αAF1, respectively). The spectra were collected either over a broad velocity range of approximately ±11 mm/s (samples αAF7, αAF10) or using a narrower scale of ±4 mm/s (αAF05, αAF1, αAF2, αAF5). In the MS for αAF2 and αAF5 only a single doublet appears, while for αAF7 and αAF10 clearly a weak sextet in addition to a dominant doublet is recognized. Preliminary fits with superpositions of a Lorentzian-shaped sextet and a doublet yielded values for the hyperfine parameters of the sextet as listed in Table 1 for subspectrum S1. These values, in particular those for the quadrupole shift δQ, are characteristic of α-Fe₃O₄. The rather low value for the hyperfine field BH (49.8 vs 51.7 T for pure bulk hematite) indicates small-particle size and a significant Al-for-Fe substitution for this α-Fe₃O₄ phase. Hence, the MS confirm the earlier mentioned phase partition in the α-(AlFe)₃O₇ solid solutions for αAF7 and αAF10.

The smaller velocity range MS show a broadened doublet with significant asymmetry in peak depths for all four samples, however, gradually lowering with increasing Fe substitution. The asymmetry might be explained by a texture effect resulting from a preferential orientation of the particles with regard to the absorber plane. According to the FEG-SEM images (Figure 4), the powders are indeed composed of large platelike particles. It is not unlikely that such morphology induces a texture that appears in the MS as an asymmetric doublet. To verify this point, MS have been measured for αAF2 and αAF5 with the absorber planes under an angle of ~54° with respect to the incident γ-rays. This angle is called “the magic-angle” and has the effect of removing the asymmetry if the latter is due to texture. The procedure of Greneche and Varret was followed (see Supporting Information, Figure S1); however, identical asymmetric line shapes were present in these magic-angle MS, hence ruling out a texture effect.

Another explanation for the asymmetry of the doublet was proposed by Corrêa et al. For powders with 10 cat % Fe-for-Al substitution, the presence of a weak doublet (ΔEQ > 1.3 mm/s) was reported in addition to the predominant Fe⁷⁺ doublet with quadrupole splitting ΔEQ ≈ 0.54 mm/s, which indeed reproduced the slight asymmetry reasonably well. The authors ascribed this weak doublet to a strongly distorted octahedral Fe⁷⁺ site in the α-alumina structure.

Attempts to fit the broad doublet component in the present spectra using superpositions of two symmetric doublets failed in the sense that inconsistent parameter values were obtained and that the adjusted line shapes showed small, but significant misfits with respect to the experimental data, in particular for the lower Fe-for-Al substitutions (see Supporting Information, Figure S2). These misfits seemed to indicate that, in addition to the two doublets, a singlet component is present as well. Thus, each of the asymmetric doublets was fitted with a superposition of a major doublet D1, a minor doublet D2, and a singlet Sg. The two doublets were described as independent quadrupole splitting distributions, while the singlet was considered as a single Lorentzian line. This model produced excellent fits of the experimental MS (solid lines in Figure 5) with relevant parameters as listed in Table 1. Some restrictions had to be imposed for the iteration procedure to reach convergence with reasonable parameter values. These restrictions are specified in the footnotes to Table 1. The residuals, i.e., the experimental minus the fitted spectra, are shown above each spectrum (Figure 5). It is evident that for the three samples with the highest Fe contents, some remaining residual signal is apparent (see also Supporting Information, Figure S3); however, no misfits are observed in the fitted spectra. The authors believe that these small residual signals are insignificant and are thought to be the result of the imposed restrictions, and therefore they do not change the conclusions of the work. The goodness-of-fit χ² for the lowest Fe contents was in the average around 1.2 while for the higher contents it was about twice as high. The line width values of the singlet component increased from ~0.30 to 0.65 mm/s as the iron content in the samples decreased. For the doublet components, which were fitted using distribution profile, the line widths of the elemental doublets are not mentioned because, as generally recognized, their values have little relevance.

It is important to stress that the existence of this singlet was confirmed by the MS obtained for a powder equivalent to αAF2 synthesized independently (i.e., in another laboratory) by the same oxinate route, which is identical to the spectrum shown in Figure 5. The actual superposition of the unresolved singlet in the MS makes the apparent quadrupole doublet of the substitutional Fe⁷⁺ asymmetric in the sense that the negative velocity peak has a slightly but significantly higher resonant absorption than the positive velocity peak.

Brown et al. applied the same three-component model to fit their MS of α-(AlFe)₃O₇ solid solutions with iron contents ranging between 2 and 10.5 cat %. They reported hyperfine parameters that are all consistent with the presently obtained values, including for the isomer shift of the singlet, i.e., δ ~ 0 mm/s. These authors considered two possible explanations for the origin of the singlet: (i) the presence of superparamagnetic inclusions of hematite in the alumina grains and (ii) Fe⁷⁺ cations...
occupying a highly regular site in a spinel indiporosity. Both explanations were eventually and rightly abandoned by the authors. They further suggested that the singlet corresponds to ferric ions and may be due to a “final remnant of a site” that occurs in the transformation process during the $\gamma \rightarrow \alpha$ phase transition. However, this is not thought to be reasonable because their reported MS parameter ($\delta \approx 0$ mm/s) does not support this.

The appearance of a singlet in the MS with isomer shift slightly different from zero at 295 K, which is characteristic of $\alpha$-Fe, prompted the idea that extremely small metallic Fe clusters may have formed within the $\alpha$-(Al$_x$Fe$_y$)$_2$O$_3$ grains. There seems to be a weak correlation between the isomer shift value and the Fe content; however, considering the experimental error in the data, this conclusion is not sound. That such clusters are indeed extremely small is proven by the observation that even at temperatures as low as 4.2 K their subspectral contribution to the MS remains as a singlet and hence they still are (super-)paramagnetic. This implies, according to a study of Bodker et al., that the clusters must have dimensions far less than 1 nm.

Moreover, it seems that the weak doublet D2 with large quadrupole splitting $\Delta E_Q \approx 1.19$ mm/s (Table 1), and hence the presence of strongly distorted Fe$^{3+}$ sites in the $\alpha$-alumina structure, is associated with the occurrence of the iron clusters. The results for the relative spectral areas RA of doublet D2 and singlet Sg (Table 1) indeed indicate that there exists a strong positive correlation between the fraction of total iron that constitutes the metallic clusters on the one hand and the fraction that is attributable to the distorted lattice sites. This finding suggests the idea that in a more or less extended neighborhood of the clusters, the octahedral sites of the $\alpha$-(Al$_x$Fe$_y$)$_2$O$_3$ structure are highly distorted so that the iron species situated within this shell of distorted sites exhibit a large quadrupole splitting.

The RA values obtained from the fitted MS of all samples are plotted against the iron content in Figure 6. The proportion of Fe nanoclusters clearly increases when the total iron content is decreased, reaching about 13% for the solid solution with only 0.5 at % of iron. Furthermore, this plot evidence beyond any doubt that there is a close association between iron clusters and highly distorted octahedral co-ordinations; in the sense that, when the proportion of clusters increases, the fraction of distorted lattice sites increases too, which is plausible if the origin of the distortion is as suggested above.

The formation of metallic iron in the process applied to produce the present $\alpha$-(Al$_x$Fe$_y$)$_2$O$_3$ solid solutions being totally unexpected and against any chemical perception, the authors applied Fe K-edge XANES measurements in an attempt to confirm the presence of iron in zero valence state. The XANES spectra of aAF2, aAF5, aAF7, aAF10, and of metallic iron are displayed in Figure 7a. The overall shape of the aAF2–aAF10 XANES spectra are comparable, whereas the spectrum of metallic iron is shifted toward lower energy. Close inspection of the energy region before 7120 eV, called the pre-edge region, reveals that the $\alpha$-(Al$_x$Fe$_y$)$_2$O$_3$ samples have two distinct pre-edge peak components sitting on the edge slope (Figure 7b). These peaks are assigned to $1s \rightarrow 3d$ transitions and used to discriminate the oxidation state and coordination number of iron. By calculation of the pre-edge peak centroid and the integrated intensities (Table 2 and Figure 8), these data can be compared with those of the model compounds with known Fe oxidation state and coordination number. For the present $\alpha$-(Al$_x$Fe$_y$)$_2$O$_3$ powders, they confirm the presence of ferric iron in 6-fold coordination sites. Furthermore, the appearance of a third component in the pre-edge region, which has been assigned to extra transitions related to Fe$_{\text{Mo}}$O$_5$ clustering, shows that no such clustering occurs here. Hence, there are no detectable hematite-like regions in the corundum lattice. The background at the pre-edge region, most clearly observable at the higher-energy side of the pre-edge peaks, increases from aAF5 to aAF2 and further to aAF10 and aAF7. Since the edge for metallic iron occurs at the same position as the pre-edge region of $\alpha$-(Al$_x$Fe$_y$)$_2$O$_3$, this feature can be used as a fingerprint for the occurrence of metallic iron in the presently studied samples.
metallic iron were performed in order to estimate the amount of metallic iron present. The results are shown in Figure 7b. Aside from the observed trend of the background intensity increase at the pre-edge region, increasing amount of metallic iron (when going from aAF5 to aAF2 and further to aAF10 and aAF7) also produces a decrease in the white line intensity and an increase in the intensity of the local minimum around 7160 eV (Figure 7a), as observed in the XANES region.

It is important to note that XANES, in contrast to MS, only allows for a semiquantitative determination of the amount of iron present in metallic state. Therefore, it may not surprise that the fractions of metallic iron in the various samples as suggested by the XANES observations are different from those found from MS (Table 1). However, it is clear that the XANES analyses confirm that zerovalent iron is indeed present in the α-(Al1.5Fe2.5)O3 grains.

An intriguing question concerns the location of the Fe nanoclusters: are they found exclusively deep inside the grains or rather concentrated in a surface shell? In an attempt to find out, an ILEEMS measurement at 295 K for the aAF2 powder was carried out. The ILEEMS (Figure 9) has the same shape and consists of the same spectral components as the transmission spectrum (Figure 5). The hyperfine parameters of all subspectral components and their relative spectral areas obtained from the ILEEMS are within the error limits identical to the respective values fitted to the transmission MS. This finding is clear evidence that the Fe nanoclusters are evenly distributed among the surface layers and the cores of the α-(Al1.5Fe2.5)O3 grains. This does not mean that Fe clusters are located on the surface but can be covered with a thin layer of alumina which is sufficient to avoid oxidation of the clusters (see here after).

**Figure 7.** (a) Experimental Fe K-edge XANES spectra of aAF2 (green line), aAF5 (blue line), aAF7 (red line), aAF10 (brown line), and metallic iron (black dotted line). (b) Blow-up of the pre-edge region. The experimental spectra (same symbols as in a) are compared with model spectra (thin dotted lines) obtained by mixing the spectrum of sample aAF5 (lowest background) with the one for Fe metal with weights ranging from 99% to 90/10. Note the evident increase of the background intensity at the pre-edge region caused by even small amount of metallic Fe.

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* Precision and accuracy of the pre-edge peak centroid energy are ± 0.05 and 0.1 eV, respectively.

**Figure 8.** Fit of the pre-edge peaks of samples aAF2, aAF5, aAF7, and aAF10. It is evident the lack of a third feature at about 7117.5 eV, typical of hematite Fe K-edge XANES spectra, which is assigned to a Fe–Fe excitation. The lack of this feature entails the absence of hematite-like domains in the corundum lattice.

It is thus believed that the combined results of MS and XANES have provided convincing arguments to conclude that metallic iron is present in the α-(Al1.5Fe2.5)O3 grains and that this metallic iron occurs as nanoclusters.

At this point, information that could be interesting concerns the thermal stability of these nanoclusters. For that purpose a batch of powder aAF2 was heated in air at 1120 °C and kept at that temperature during ten hours. After cooling down the sample to room temperature, its measured MS turned out to be...
Figure 9. ILEEMS5 spectrum collected at room temperature for sample aAlF.

The weak doublet with large quadrupole splitting is shaded in olive while the singlet due to Fe clusters is shaded in red and the major doublet shaded in blue.

...of the composite of the same components as those observed in the spectrum of the original aAlF2 (Figure 5), with roughly equal subspectral areas. It was further experienced that when heating was performed at 1300 °C, a few no changes are obvious in the subsequently acquired 295 K MS (see Supporting Information, Figure S4). These results indicate that the iron nanoclusters are extremely stable against heating for long times at relatively high temperatures, which is in agreement with the observations by Brown et al. 3 Moreover, it is interesting to note that, for Fe/Cr-Al2O3 and carbon nanotube-Fe-Al2O3 powders prepared by reduction in H2 or He—CH4 of similar corundum solid solutions, 22,23 the oxidation in air of the metal particles (<10 nm in diameter) located inside the Al2O3 grains was found to take place at the temperature as high as 1200 °C.

Taking into account that the calculation of the γ-(Al15Fe21O28) powders for the preparation of the Fe nanoclusters is somehow associated with the phase transition, two samples of γ-(Cr13Fe21O28) with different amounts of iron were prepared by decomposition of the mixed-oxide precursors. The obtained MS at 295 K (not shown) clearly consist of a single narrow Fe3+ doublet (line width of ~0.27 mm/s) with no significant asymmetry. As these powders were obtained directly as α-modification and thus a γ → α phase transition is involved, in contrast to the Fe nanoclusters in the latter solid solutions is related to the γ → α transition. What the real driving force may be, however, remains unclear so far.

Conclusions

The aim of this paper was to shed some light into a matter which was reported several times but was never satisfactorily accounted for, regarding the unexpected asymmetry of the characteristic Mössbauer doublet representing Fe3+ ions substituting for Al3+ ions in the corundum lattice of α-(Al15Fe21O28) solid solutions. The Mössbauer spectra of α-(Al15Fe21O28) powders obtained by the calcination in air of the corresponding γ-(Al15Fe21O28) powders were found to be composed, in addition to the expected Fe3+ doublet due to the Fe3+ ions substituting for Al3+ ions in octahedral sites, of a broad second doublet characteristic of a very distorted octahedral site for Fe3+ and a singlet attributable to α-Fe, suggesting for the first time the presence of metallic iron nanoclusters within the solid solution grains. As no magnetic ordering occurs within the nanoclusters at temperatures as low as 4.2 K, it is believed that they consist of only a few number of atoms. ILEEMS studies showed that the Fe nanoclusters are evenly distributed among the surface layers and the cores of the α-(Al15Fe21O28) grains. Fe K-edge XANES measurements allowed ascertainment of the absence of hematite-like domains in the corundum lattice and further confirmed the occurrence of metallic iron. The proportion of Fe nanoclusters increases when the total iron content is decreased, as does the proportion of the very distorted octahedral site, pointing out to a close association between the nanoclusters and distorted sites. This could suggest that the distorted octahedral site is located around the iron clusters. The formation of the metallic Fe nanoclusters in the α-(Al15Fe21O28) grains is thought to be a consequence of the γ → α phase transition which implies structural rearrangement on both the cationic and anionic sublattices.

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Supporting Information Available: Figure S1: Mössbauer spectra of sample aAlF2 showing the absence of texture effect in the powder. Figure S2: Mössbauer spectra of two of the α-(Al15Fe21O28) samples and the respective spectral fitting residuals showing the misfits. Figure S3: Mössbauer spectrum of sample aAlF7 with the remaining residual signal. Figure S4: Mössbauer spectrum of sample aAlF2 heated during 10 h at 1300 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

Fe Nanoclusters in $\alpha-(\text{AlFe})_2\text{O}_3$ Solid Solutions


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Paper III

Catalytic chemical vapor deposition synthesis of single- and double-walled carbon nanotubes from $\alpha$-$(\text{Al}_{1-x}\text{Fe}_x)_2\text{O}_3$ powders and self-supported foams

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Catalytic chemical vapor deposition synthesis of single- and double-walled carbon nanotubes from \(\alpha-(Al_{1-x}Fe_x)_2O_3\) powders and self-supported foams

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ABSTRACT
An investigation of the potential interest of \(\alpha\)-alumina-hematite foams, as opposed to powders, as starting materials for the synthesis of carbon nanotubes (CNTs) by catalytic chemical vapor deposition method was performed. The oxide powders and foams as well as the corresponding CNT-\(\alpha\)-Fe\(_2\)O\(_3\) composite powders and foams are studied by X-ray diffraction, specific surface area measurements, electron microscopy, Raman spectroscopy and Mössbauer spectroscopy. The latter technique revealed that four components (corresponding to \(\alpha\)-Fe, \(\gamma\)-Fe, \(\gamma\)-Fe-C and Fe\(_3\)Al) were present in the Mössbauer spectra of the composite powders, and that an additional sextet, possibly due to an \(\alpha\)-Fe\(_3\)Al\(_2\) alloy, is also present in the Mössbauer spectra of the composite foams. Contrary to some expectations, using foams do not lead to an easier reduction and thus to the formation of more \(\alpha\)-Fe, \(\gamma\)-Fe-C and/or \(\gamma\)-Fe-C potentially active particles for the formation of CNTs, and hence to no gain in the quantity of CNTs. However, using foams as starting materials strongly favours the selectivity of the method towards SWCNTs (60% SWCNTs and 40% DWNTs) compared to what is obtained using powders (5% SWCNTs, 65% DWNTs and 30% MWNTs).

1. Introduction
The synthesis of carbon nanotubes (CNTs) by catalytic chemical vapor deposition (CCVD) is based on the catalytic decomposition of carbonaceous gases such as CH\(_4\) on transition metal (usually Fe or Co) nanoparticles. The nanoparticles are either supported by a substrate, or held in suspension in the gas stream. A critical survey of the bibliography [1] revealed that many different CCVD routes can succeed provided all parameters related to the metal source are adapted to all parameters related to the carbon source, at the appropriate synthesis temperature. Indeed, the critical step is the formation of metal nanoparticles, which must have a size (0.4–5 nm) adequate for the formation of single-wall CNTs (SWCNTs) and double-wall CNTs (DWNTs) (2–3) at a temperature (usually in the range 600–1100 °C) making possible the catalytic (as opposed to thermal) decomposition of the carbonaceous gas.

One method [4], ensuring that the metal particles do not grow too much, involves the reduction in H\(_2\)-CH\(_4\) of
alumina-hematite solid solutions, first producing nanometric Fe particles that are active for the decomposition of CH₄, thus producing CNT-Fe-Al₂O₃ composite powders. The influence of the characteristics of the solid solutions upon the synthesis of CNTs has been the subject of intensive research. In particular, in order to increase the quantity of CNTs, it is desirable that there are more Fe nanoparticles on the surface of the oxide grains. Increasing the geometrical surface area by a grinding which decreases the grain size of the starting powder of alumina-hematite solid solution was found to be useful, possibly because of the much higher packing of the ground powder. When using the high-specific-surface-area amorphous or transition solid solutions prepared from the mixed-oxalate decomposition and calcination, it was found [6] that some undesirable carbon species are entrapped within the Al₂O₃ grains upon the crystallization into the corundum (α) form which occurs during the H₂-CH₄ reduction step. Thus, the aim of this paper is to investigate a new way to prepare α-alumina-hematite starting materials. This will involve the preparation of self-supported foams. The advantage of the shaping into a foam, as opposed to a powder, is that the porous oxide solid solution presents a very low packing, which should permit firstly to obtain more active surface area and therefore catalyst nanoparticles and secondly to maintain free space that will allow a good diffusion of CH₄. This route has given promising results when applied to catalytic materials based on (Mg,Co)Al₂O₃ [7] and (Mg,Co)MnO [8]. CNTs-Fe-Al₂O₃ composite powders and foams will be studied by electron microscopy, Raman spectroscopy and Mössbauer spectroscopy.

2. Experimental

2.1. Preparation of powders and self-supported foams

α-(Al₁₋ₓFeₓ)₂O₃ (corundum) powders (x = 0.02, 0.05, 0.07, 0.10) were prepared by decomposition and calcination of the AlFe oxalate precursors whose preparation is detailed elsewhere [8]. The powders were code-named as PX, where X represents the iron content (0.2, 0.5, 0.7 and 1.0 wt%) in the solid solution.

About 3 g of each α-(Al₁₋ₓFeₓ)₂O₃ powder was mixed with 0.045 g of dispersant (BEOCOSTAT C213, CICA France), which represents 1 mg of dispersant/m² of powder, diluted in about 10 ml of ethanol. The mixture was kept under magnetic stirring for about 10 min for homogenization. The so-obtained dispersant-powder mixture was attrition-milled (2000 rpm, 3 h) using a Nylon vessel and rotor, and alumina balls (200-300 μm in diameter). The ratio between the powder volume and the volume of the balls was 0.5. After attrition milling, the powder was separated from the alumina balls by rinsing in ethanol and filtering. The composition of the resulting slurry was adjusted to about 35 wt% dispersant-powder mixture and 65 wt% ethanol. A polyurethane foam (80 pores per inch, 60 × 30 × 20 mm³) was impregnated with the slurry. The impregnated foam was mechanically pressed several times in order to eliminate the excess slurry. It was then dried overnight at room temperature and calcinated in air (600 °C, 150 °C/h, 60 min) in order to burn all organics, producing the self-supported α-(Al₁₋ₓFeₓ)₂O₃ foams. These foams were code-named as FX, after the corresponding powder PX. Note that only three foams were prepared (P2, P5 and P7).

2.2. Synthesis of carbon nanotubes

The solid solution powders and foams were reduced in a H₂-CH₄ (20 mol% CH₄) gas mixture in a silica reactor (inner diameter 56 mm, length of the heating zone 200 mm). The heating and the cooling rate to the desired temperature (1025 °C) and back to room temperature was 5 °C/min. No dwell time was applied at 1025 °C. The flowing gas was dried on P₂O₅ and its composition was regulated by mass-flow controllers. The total flow rate was 15 l/h. The so-obtained CNTs-Fe-Al₂O₃ composite powders and foams are code-named as PXR and FXR, respectively.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded in the range 10–70° (2θ) with a Bruker D4 Endeavor diffractometer operating with Cu Kα radiation. Counts were recorded every 0.02° (2θ). The specific surface area of the oxide powders and foams was measured by the BET method (Micromeritics Flow Sorb II 2300) using nitrogen adsorption at liquid nitrogen temperature. This instrument gives a value from one point (i.e. one adsorbate pressure) and requires calibration. The reproducibility of the results is in the ±3% range. Mössbauer spectra at room temperature (295 K) and at 10 K were collected using spectrometers operating at constant acceleration mode with triangular reference signals. 57Co(Rh) sources were used. All Mössbauer spectra were analyzed in terms of model-independent distributions of hyperfine parameter values and numerical data quoted hereafter refer to maximum-probability values [10]. Isomer shifts are referenced with respect to α-Fe at room temperature. The carbon content (Cₐ) in the composite powders and foams was measured by the flash combustion method with an accuracy of ±2%. Raman spectra were recorded using a LabRAM 800 Jobin–Yvon spectrometer (632.82 nm) and were averaged on three spectra. The powders and foams were observed by field-emission-gun scanning electron microscopy SEM (FEG-SEM, JEOL JSM 6700F). The observations were performed with a tension of 5 kv and a work distance between 4.0 and 6.2 mm. Composite specimens were plated with Pt before FEG-SEM observations. High-resolution transmission electron microscopy (HREM) was performed with a JEOL JEM 2100F microscope operated at 200 kV. The samples were slightly sonicated in ethanol, and a drop of the suspension was deposited onto a holey carbon grid.

3. Results and discussion

3.1. Oxide powders and foams

The XRD patterns of the PX powders (not shown) show peaks characteristic of well-crystallized corundum solid solution. For P10, however, several weak additional lines corresponding to hematite (α-Fe₂O₃) are observed. This reveals that for this
Table 1 - Hyperfine parameters at room temperature for the α-(Al₄₋ₓFeₓ)O₃ powders [9].

<table>
<thead>
<tr>
<th>Sample</th>
<th>D1</th>
<th>D2</th>
<th>Sg</th>
<th>S1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AE₂</td>
<td>δ₁</td>
<td>RA (%)</td>
<td>δ₁</td>
</tr>
<tr>
<td>P2</td>
<td>0.54</td>
<td>0.30</td>
<td>63</td>
<td>1.18</td>
</tr>
<tr>
<td>P5</td>
<td>0.53</td>
<td>0.30</td>
<td>85</td>
<td>1.18</td>
</tr>
<tr>
<td>P7</td>
<td>0.54</td>
<td>0.29</td>
<td>88</td>
<td>1.20</td>
</tr>
<tr>
<td>P10</td>
<td>0.54</td>
<td>0.29</td>
<td>85</td>
<td>1.20</td>
</tr>
</tbody>
</table>

B₀H, Hyperfine field at maximum of the distribution (T). Z₁₂, quadrupole shifts (mm/s); AE₂, quadrupole splitting (mm/s); δ, isomer shifts (mm/s); RA, relative spectral area (%). The values of isomer shifts are with reference to metallic iron.

a The isomer shifts of D1 and D2 were coupled.
b Fixed parameters.

The Mössbauer spectra (not shown) of the α-(Al₄₋ₓFeₓ)O₃ powders were studied in detail elsewhere [9]. They are composed of a dominant Fe⁺⁺ quadrupole doublet with quadrupole splitting AE₂ = 0.54 mm/s besides two other weaker components, i.e., a singlet and another quadrupole doublet with AE₂ = 1.2 mm/s. Additionally, the presence of a weak sextet characteristic of Fe²⁺O₃⁻ is observed for samples P7 and P10. The Mössbauer spectra parameters are listed in Table 1 [9]. The dominant doublet was attributed to Fe⁺⁺ ions substituting for Al³⁺ ions in the corundum structure. The singlet was ascribed, on the basis of its isomer shift value, to extremely small metallic Fe nanoclusters that for some yet unknown reason may have formed within the solid solution granules, which is an unusual result that is discussed elsewhere in detail [9]. However, the amount of iron involved is very minor (Table 1) and the specimens are nevertheless considered as solid solutions. The isomer shift obtained for the weak doublet (−0.3 mm/s at 295 K) points at an Fe⁺⁺ species in an octahedral co-ordination. Its high quadrupole splitting (AE₂ = 1.2 mm/s) implies a strong deformation of the octahedral symmetry of the involved site. As discussed elsewhere [9], these strongly deformed sites could most likely be associated to the presence of the metallic nanoclusters within the solid solution granules. The presence of the weak α-Fe₂O₃ sextet for P7 and P10 indicates that some phase partitioning into an alumina-rich corundum phase and a hematite-rich phase occurred during the calcination step. Regarding the self-supported foams, there is no reason to suspect that the process used in the present work produced any change in the distribution of the Fe⁺⁺ ions.

Fig. 1 - Typical FEG-SEM images showing the α-(Al₄₋ₓFeₓ)O₃ powders (a and b) and the walls of the corresponding foams (c and d).
Fig. 2 - MS of the CNTs–Fe–Al₂O₃ powders measured at 295 K (left) and 15 K (right).

Table 2 - Mössbauer results of the CNTs–Fe/alumina powders at 295 K and 15 K. The quadrupole shifts ($\Delta E_Q$), quadrupole splitting ($\delta E_Q$) and isomer shifts ($\delta$) are given in mm/s, the hyperfine fields ($B_H$) are in T and the relative spectral areas (RA) are given in %. The values of isomer shifts are with reference to metallic iron.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe/C</th>
<th>α-Fe</th>
<th>γ-Fe</th>
<th>(A₁Fe₃O₄)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$B_H$</td>
<td>$\Delta E_Q$</td>
<td>$\delta$</td>
<td>RA</td>
</tr>
<tr>
<td>295 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P2R</td>
<td>20.7</td>
<td>0.07</td>
<td>0.19</td>
<td>15</td>
</tr>
<tr>
<td>P3R</td>
<td>20.7</td>
<td>0.02</td>
<td>0.51</td>
<td>16</td>
</tr>
<tr>
<td>P7R</td>
<td>20.7</td>
<td>0.04</td>
<td>0.20</td>
<td>22</td>
</tr>
<tr>
<td>P10R</td>
<td>20.8</td>
<td>0.04</td>
<td>0.20</td>
<td>24</td>
</tr>
<tr>
<td>15 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P2R</td>
<td>25.6</td>
<td>0.03</td>
<td>0.36</td>
<td>19</td>
</tr>
<tr>
<td>P3R</td>
<td>25.6</td>
<td>0.01</td>
<td>0.35</td>
<td>16</td>
</tr>
<tr>
<td>P7R</td>
<td>25.8</td>
<td>0.00</td>
<td>0.33</td>
<td>21</td>
</tr>
<tr>
<td>P10R</td>
<td>25.7</td>
<td>0.01</td>
<td>0.33</td>
<td>24</td>
</tr>
</tbody>
</table>

a Also present is a weak doublet with $\Delta E_Q$ about 1.58 mm/s, $\delta = 0.79$ mm/s and RA ~11%.
b Also present is a weak doublet with $\Delta E_Q$ about 1.58 mm/s, $\delta = 0.79$ mm/s and RA ~11%.
c Also present is a weak doublet with $\Delta E_Q$ about 1.52 mm/s, $\delta = 0.49$ mm/s and RA ~10%.
d Also present is a weak doublet with $\Delta E_Q$ about 1.53 mm/s, $\delta = 0.81$ mm/s and RA ~6%.
e Fixed parameter value.
FEG-SEM images (Fig. 1a and b) of the powders reveal that they are made up of 2-5 μm grains assembled into tabular-like aggregates. However, the observation of smaller entities and of side-views of the tabular-grains reveals the so-called vermicular microstructure with much looser aggregates made up of 0.2-0.5 μm primary grains or crystals. The BET specific surface area of these powders is in the range 4.4-6.0 m²/g, in good agreement with the usual values for corundum. Interestingly, FEG-SEM images (Fig. 1c and d) of the walls of the self-supported foams reveal a much more homogeneous microstructure, with grains generally smaller than 0.5 μm and appearing relatively densely packed. The BET specific surface area of the foams is in the range 10.1-18.7 m²/g, the increase as compared to the powders probably reflecting the lower average grain size.

3.2. Composite powders and foams

Analyses of the XRD patterns (see Supplementary Data, Figure S1) of the PXR powders reveals the pattern of a corundum

![Graphical representation](image)

**Fig. 3** - MS of the CNTs-Fe-Al₂O₃ foams (F3R and F7R) measured at 295 K (left) and 15 K (right).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe₃C</th>
<th>α-Fe</th>
<th>γ-Fe-C</th>
<th>(Al,Fe)O₃</th>
<th>Fe₁₋ₓCₓ</th>
<th>δ</th>
<th>RA</th>
<th>δ</th>
<th>RA</th>
<th>δ</th>
<th>RA</th>
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<tr>
<td>F3R</td>
<td>30.2</td>
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<td>0.19</td>
<td>8</td>
<td>0.09</td>
<td>0.55</td>
<td>0.32</td>
<td>27</td>
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<td>33</td>
<td>0.56</td>
<td>0.33</td>
<td>25</td>
<td>0.56</td>
<td>0.33</td>
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<tr>
<td>FSR</td>
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<td>0.19</td>
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<td>0.33</td>
<td>19</td>
<td>0.56</td>
<td>0.33</td>
<td>23</td>
<td>0.56</td>
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<td>19</td>
<td>0.56</td>
<td>0.33</td>
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<tr>
<td>F7R</td>
<td>20.0</td>
<td>0.03</td>
<td>0.10</td>
<td>15</td>
<td>33.5</td>
<td>0.00</td>
<td>0.56</td>
<td>0.33</td>
<td>19</td>
<td>0.56</td>
<td>0.33</td>
<td>23</td>
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<td>15 K</td>
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<tr>
<td>F3R</td>
<td>24.8</td>
<td>0.03</td>
<td>0.31</td>
<td>14</td>
<td>34.6</td>
<td>0.11</td>
<td>10</td>
<td>0.91</td>
<td>18</td>
<td>0.55</td>
<td>0.42</td>
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<tr>
<td>FSR</td>
<td>34.7</td>
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<td>0.31</td>
<td>12</td>
<td>34.7</td>
<td>0.12</td>
<td>31</td>
<td>0.91</td>
<td>31</td>
<td>0.56</td>
<td>0.42</td>
<td>17</td>
<td>29.0</td>
<td>0.24</td>
<td>9</td>
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<td></td>
</tr>
<tr>
<td>F7R</td>
<td>24.7</td>
<td>0.03</td>
<td>0.31</td>
<td>16</td>
<td>34.7</td>
<td>0.12</td>
<td>38</td>
<td>0.91</td>
<td>24</td>
<td>0.57</td>
<td>0.43</td>
<td>13</td>
<td>28.7</td>
<td>0.24</td>
<td>9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Fixed value.
Fig. 4 - High-frequency range of the Raman spectra (632.82 nm) showing the D and G bands for the CNTs-Fe-Al₂O₃ powders and (inset) the corresponding low-frequency range showing the RBM peaks.

Fig. 5 - FEG-SEM images of the powders: P2R (a), P5R (b), P7R (c) and P10R (d).
phase and the peaks of Fe$_3$C and α-Fe with increasing intensities upon the increasing iron content. It is difficult to separate the XRD patterns of Fe$_3$C and α-Fe because the respective main peaks are rather broad and strongly overlapping. γ-Fe may also be present, but cannot be observed because the main γ-Fe peak (d$_{223}$ = 0.208 nm) is masked by the corundum (d$_{223}$ = 0.209 nm) and Fe$_3$C (d$_{223}$ = 0.210 nm) peaks. As expected, the XRD patterns of the F3R foams (see Supplementary Data, Figure S2) show features essentially similar to those observed for the F3R powders.

The Mössbauer spectra collected at 295 K and 15 K are reproduced in Fig. 2 left and right, respectively. Three of the subspectral components found in the Mössbauer spectra of the parent oxides have vanished: the α-Fe$_2$O$_3$ sextet, the weak Fe$^{3+}$ doublet and the singlet due to metallic Fe clusters. Moreover, only part of the main Fe$^{3+}$ doublet has remained, the extent depending on the initial iron concentration, whilst three other components have appeared. Thus, four components were found to be required to obtain adequate fits of these spectra: (i) an outer sextet with hyperfine parameters typical of the α-Fe phase; (ii) an inner sextet that can be attributed to Fe$_3$C; (iii) a central singlet due to a γ-Fe phase, maybe alloyed with carbon; and (iv) a doublet that can be ascribed to Fe$^{3+}$ species substituting in the Al$_2$O$_3$ structure. For samples F2R and F5R, meticulous fitting attempts of their Mössbauer spectra have led to the conclusion that an additional, but weak (<1% of total absorption area) and rather ill-defined doublet has to be included in the model. Its quadrupole splitting $\Delta E_Q$ was found to be $\sim$1.6 mm/s and its isomer shift $\delta$ of 0.8 mm/s at 295 K. This latter value is neither typical of Fe$^{3+}$, nor of Fe$^{3+}$, but is rather in between. Moreover, the $\Delta E_Q$ value is unusually high for Fe$^{3+}$. It is proposed that the resolved broad doublet is actually an approximation for the spectrum of a hercynite phase (FeAl$_2$O$_4$). The Mössbauer spectrum of such spinel-type compounds is composed of several quadrupole doublets arising from Fe$^{3+}$ and from Fe$^{3+}$, as such rendering their Mössbauer spectrum very complicated and highly unresolved [11-15]. Consequently, when fitting such a composition of Fe$^{3+}$ and Fe$^{3+}$ doublets by one single doublet, one obtains a broad line width and hyperfine parameters with values that are intermediate between those characteristic for Fe$^{3+}$ and Fe$^{3+}$, respectively.

The relevant numerical data resulting from the adjustments of the respective spectra are listed in Table 2. The relative spectral areas (RA) of the various components (Table 2), change significantly when the temperature is lowered from 295 K to 15 K. This can be due either to superparamagnetic effects in some of the constituents at 295 K, or to the weaker resolution of the respective subspectra, making the derived Mössbauer parameters, in particular the RA values, less reliable. The occurrence of superparamagnetism is a well-known property of magnetic small particles ([16] and references therein). In the Mössbauer spectra, this phenomenon is reflected in the collapse of the magnetically split spectrum into an apparently paramagnetic doublet or singlet at temperatures lower than the respective Curie or Néel point of the involved material in bulk appearance. This collapse is due to fast relaxation of the magnetization vector as a whole. It is reasonable to consider that the Fe phases present in the composites exhibit relatively broad particle-size distributions.

Consequently, some of these phases may present a superparamagnetic effect at relatively high temperatures, resulting in the appearance of a quadrupole doublet or a singlet in the Mössbauer spectra acquired at these temperatures. In view of this feature it could be that part of the Fe$^{3+}$ doublet and/or the singlet presently observed at the higher temperature (295 K) is actually due to Fe constituents that at 15 K are experienced as being magnetic, i.e., as a sextet. In this sense, one may raise doubts about the validity of the Mössbauer parameters obtained for the Mössbauer spectra at 295 K, in particular the relative spectral areas RA. For this reason, only the data referring to 15 K are thought to be reliable and useful. The main differences between the four powders concern the RA values for the (Al,Fe)$_2$O$_3$ doublet and the α-Fe sextet. The RA value for the (Al,Fe)$_2$O$_3$ doublet steadily decreases from F2R to F1R.

Fig. 6 - FEG-SEM images of the foams: F2R (a), F5R (b) and F7R (c).
showing that the reduction is comparatively easier when the total iron content is increased. The α-Fe sextet is significantly more abundant for F7R and P10R than for F2R and P5R, which could be a consequence of the easier reduction process and could also reflect the presence of a hematite-rich phase (Table 1) in the corresponding F7 and P10 powders.

Typical Mössbauer spectra recorded at 295 K and 15 K for the ZrN foams are reproduced in Fig. 3 and the relevant Mössbauer parameters are reported in Table 3. Some constraints had to be imposed to the fit procedure. They are indicated in the footnotes to Table 3. In the applied fitting model, generally five patterns were included: the four components (corresponding to α-Fe, Fe₃C, γ-Fe-C and Fe⁺) that were also present in the Mössbauer spectra of the FZR powders, and an additional sextet. This later component is possibly due to an αFe₃C₅ alloy [17]. However, this fifth component could not be resolved from the 295 K spectrum for F2R, and also the α-Fe subspectrum was not detected in this latter spectrum. Note that the relative abundance of the (Al,Fe)₂O₃ doublet for F7R (53%) is much higher than for F2R (27%), indicating that the reduction was significantly more difficult for the former specimen. The RA values for F5R and F7R are similar to those for P5R and P7R. These results reveal that contrary to some expectations, the lower grain size and higher specific surface area of the starting oxide foams do not lead to an easier reduction and thus to the formation of

Fig. 7—HRTEM images for powder P5R.
more α-Fe, Fe-C and/or γ-Fe-C potentially active particles for the formation of CNTs. This could be due to the higher packing of the solid solution grains in the walls of the foam.

The carbon content (C_1) was found equal to 0.6, 1.0, 1.9 and 3.3 wt% for P2R, PSR, P3R and P4R, respectively. This evolution is in agreement with earlier results [18] obtained with powders by the oxalate (not oxinate) route, although the values are lower. This difference arises because in the earlier study [18], there was a dwell time of 4 h at the maximum reduction temperature, whereas no dwell time was applied for the present study. The carbon content was found equal to 0.8, 1.4 and 1.5 wt% for F2R, F3R and F4R, respectively. These values are not much different than those measured for the PXR powders, which is in line with the conclusion of the above Mössbauer spectroscopic study.

The high-frequency range (1200–1800 cm⁻¹) of the Raman spectra (Fig. 4) shows the D band (ca. 1330 cm⁻¹) and the G band (ca. 1580 cm⁻¹). The ratio between the intensity of the D band and the G band, I_DG, is very high for P2R (180%) and much lower (close to 30%) for the other three powders. An increasing I_DG value corresponds to a higher proportion of sp²-like carbon, which is generally attributed to the presence of more structural defects. In addition, the G band for P2R shows a shoulder at higher frequency (ca. 1615 cm⁻¹), which is typical of defective graphite-like materials [19]. The presence of radial-breathing-modes (RBM) peaks in the low-frequency range (100–300 cm⁻¹) of the spectrum (inset in Fig. 4), the frequencies of which are inversely proportional to the CNT diameters, is usually the sign of the presence of small-diameter CNTs, such as SWCNTs and DWCNTs. Only very weak RBM peaks are observed for P2R. Note however that the Raman process is influenced by optical resonance and it is thus impossible to detect all present CNTs using only one wavelength. Moreover, the peak intensities do not reflect the real amount of individual CNTs because of the resonance effect which amplifies the Raman signal from certain CNT. The Raman spectra (see Supplementary Data, Figure S3) of the PXR composite foams clearly reveal a decrease in the intensity ratio I_DG with increasing Fe content (88, 66 and 33% for F2R, F3R and F4R, respectively). Compared to the corresponding PXR powders, the I_DG values are much lower, higher and similar for F2R, F3R and F4R, respectively. RBM peaks are detected for all three composite foams.

FESEM images (Fig. 5) of the PXR specimens reveal the presence of long, flexible filaments, with a smooth and regular surface, on the surface of the oxide grains and bridging several grains. The quantity of such filaments increases with increasing X. All filaments have a diameter smaller than 30 nm and a length of the order of some tens of micrometers. From earlier results, it is known that such filaments are isolated CNTs and/or CNTs bundles. Spherical particles 5–20 nm in diameter that may be α-Fe, Fe-C and/or γ-Fe-C (some of which are arrowed on Fig. 5) are observed at the surface of the alumina grains. Most of these particles do not appear to be connected to a CNT, indicating that they have been inactive for the formation of CNT. It is interesting to note that the presence of undesirable thick, short carbon nanofibers is not observed. FESEM images (Fig. 6) of the PXR specimens reveal features essentially similar to what is observed for the PXR samples.

Typical HRTEM images collected for sample PSR are shown in Fig. 7. The images show CNT bundles (Fig. 7a and d), DWCNTs (Fig. 7b and e) and CNTs with four walls (Fig. 7c). Carbon nanofibers partly filled with a metal particle (Fig. 7f) are very rarely observed, in agreement with the FESEM results. An inactive particle (α-Fe, Fe-C or γ-Fe-C) covered by several graphene layers is shown in Fig. 7g. Fig. 8 presents histograms of the number of walls and diameter distributions, which were obtained by measuring CNTs on similar HRTEM images for sample PSR. The distribution of the number of walls (Fig. 8a) shows that about 65% of CNTs are DWCNTs. Most of the other CNTs have three, four or five walls, the SWCNTs accounting only for less than 5%. The diameter distribution (Fig. 8b) spans a relatively broad range. The inner diameter averages at ~2.7 nm and the outer diameter at ~4.4 nm. HRTEM images (Fig. 9) were collected for sample FSR. Note that the poorly ordered carbon observed at the surface of the CNTs originates from CNTs damaged under the electron beam. The important difference compared to PSR is that SWCNTs (Fig. 9a and b) and DWCNTs (Fig. 9c) appear to be considerably more abundant than in PSR, to the detriment of MWCNTs. Indeed, the histogram of the number of wall indicates 60% SWCNTs and 40% DWCNTs (see Supplementary Data, Figure S4). This finding is in agreement with previous results [7,8] showing that the selectivity of the method towards SWCNTs is much higher when the starting material is in the form of a foam as opposed to a powder. The XRD and Mössbauer spectroscopic studies do not seem to reveal differences.
that could account for this, prompting out the need for future studies.

4. Conclusions

The Mössbauer spectroscopy technique revealed that four components (corresponding to α-Fe, Fe₃C, γ-Fe-C and Fe⁺) were present in the Mössbauer spectra of the composite powders, and that an additional sextet, possibly due to an Fe₁₋₂γC alloy, is also present in the spectra of the composite foams. Contrary to some expectations, the lower grain size and higher specific surface area of the starting oxide foams compared to the powders do not lead to an easier reduction and thus to the formation of more α-Fe, Fe₃C and/or γ-Fe-C potentially active particles for the formation of CNTs. This could be due to the higher packing of the solid solution grains in the walls of the foam. Thus, there is no gain in the quantity of CNTs, but HRTEM images interestingly revealed that the selectivity of the method towards SWCNTs is much higher when the starting material is in the form of foam (60% SWCNTs and 40% DWCNTs) as opposed to a powder (5% SWCNTs, 65% DWCNTs and 30% MWCNTs).

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Appendix A. Supplementary data


REFERENCES


In situ high-temperature Mössbauer spectroscopic study of carbon nanotube-Fe-Al$_2$O$_3$ nanocomposite powder

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In situ high-temperature Mössbauer spectroscopic study of carbon nanotube-Fe-Al$_2$O$_3$ nanocomposite powder

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The oxidation of a carbon nanotube-Fe-Al$_2$O$_3$ nanocomposite powder was investigated using notably thermogravimetric analysis, room temperature transmission and emission Mössbauer spectroscopy and, for the first time, in-situ high-temperature transmission Mössbauer spectroscopy. The first weight gain (150-300°C) was attributed to the oxidation into hematite of the $\alpha$-Fe and Fe$_3$C particles located at the surface and in the open porosity of the alumina grains. The 25 nm hematite particles are superparamagnetic at 250°C or above. A weight loss (300-540°C) corresponds to the oxidation of carbon nanotubes and graphene layers surrounding the nanoparticles. The graphene layers surrounding $\gamma$-Fe-C particles are progressively oxidized and a very thin hematite layer is formed at the surface of the particles, preventing their complete oxidation while helping to retain the face-centered cubic structure. Finally, two weight gains (670 and 1120°C) correspond to the oxidation of the intragranular $\alpha$-Fe particles and the $\gamma$-Fe-C particles.

1 INTRODUCTION

Although many studies on the thermal stability of samples of carbon nanotubes (CNT) have been reported, most of them are performed on purified specimens and focus on the oxidation of the CNTs. By contrast, relatively few thermal stability studies have been reported on the as-produced specimens, i.e. still containing the catalyst and substrate [1-5] or on CNT-oxides mixtures prepared on purpose [6,7]. The synthesis of CNTs by catalytic chemical vapor deposition (CCVD) is based on the catalytic decomposition of carbonaceous gases on transition metal nanoparticles which quite often are made up of iron, iron-cobalt, iron-nickel or iron-molybdenum alloys or mixtures. $^{57}$Fe Mössbauer spectroscopy (MS) offers several advantages for studies of iron-containing compounds. The spectra, and parameters derived from these, are very sensitive to electronic, magnetic and structural characteristics of the probed material and as such, MS is a useful tool for phase identification and quantification of mixtures of Fe-bearing materials. The aim of this paper is to study the oxidation in air of a CNT-Fe-Al$_2$O$_3$ nanocomposite powder using notably thermogravimetric analysis and, for the first time to the best of our knowledge, in-situ high temperature MS to follow the evolution of the various iron phases in the different stages of the oxidation process of the nanocomposite powder.

2 EXPERIMENTAL

Materials

A CNT-Fe-Al$_2$O$_3$ nanocomposite powder (henceforward codenamed as C0) was obtained by the reduction of an $\alpha$-(Al$_{0.93}$Fe$_{0.07}$)$_2$O$_3$ powder in a H$_2$-CH$_4$
gas mixture as described elsewhere [8]. Briefly, the \( \alpha-(\text{Al}_{0.93}\text{Fe}_{0.07})_2\text{O}_3 \) powder was prepared by decomposition and calcination of the mixed oxinate precursors. It was reduced in a \( \text{H}_2-\text{CH}_4 \) (20 mol% \( \text{CH}_4 \)) gas mixture. The heating and the cooling rate to the desired temperature (1025°C) and back to room temperature was 5°C/min. No dwell time was applied at 1025°C. The so-obtained CNT-Fe-\( \text{Al}_2\text{O}_3 \) nanocomposite powder was studied in detail by a variety of techniques [8] the results of which are summarized in the following. The carbon content \( (C_n) \) was found equal to 1.6 wt.%.

The ratio between the intensity of the D band (ca. 1320 cm\(^{-1}\)) and the G band (ca. 1580 cm\(^{-1}\)) of the high-frequency range of the Raman spectra, \( I_{\text{D/G}} \), is equal to about 30%. An increasing \( I_{\text{D/G}} \) value corresponds to a higher proportion of sp\(^3\)-like carbon, which is generally attributed to the presence of more structural defects. The presence of radial-breathing-modes (RBM) peaks in the low-frequency range (100-300 cm\(^{-1}\)) of the spectrum, the frequencies of which are inversely proportional to the CNT diameters, reveals the presence of small-diameter CNTs, such as SWNTs and DWNTs. A typical FEG-SEM image (Fig. 1) reveals the presence of long, flexible filaments, with a smooth and regular surface, on the surface of the oxide grains and bridging several grains. All filaments have a diameter smaller than 30 nm and a length of the order of some tens of micrometers. From earlier results, it is known that such filaments are isolated CNTs and/or CNTs bundles. Spherical particles 5-20 nm in diameter, that may be \( \alpha\)-Fe, Fe\(_3\)C and/or \( \gamma\)-Fe-C (some of which are arrowed on Fig. 1) are observed at the surface of the alumina grains. Most of these particles are covered by a few graphene layers and do not appear to be connected to a CNT, indicating that they have been inactive for the formation of CNT. It is interesting to note that the presence of undesirable thick, short carbon nanofibers is rarely observed.

![Fig. 1. Typical FEG-SEM image of the CNT-Fe-\( \text{Al}_2\text{O}_3 \) nanocomposite powder. The arrows point \( \alpha\)-Fe, Fe\(_3\)C and/or \( \gamma\)-Fe-C nanoparticles at the surface of the alumina grains.](image)

**Methods**

Thermogravimetric analysis (TGA) of the CNT-Fe-\( \text{Al}_2\text{O}_3 \) nanocomposite powder was performed in a SETARAM TAG 24 module (simultaneous symmetrical thermoanlyser). The powder (~ 22 mg) was heated (1°C/min) from 25 to 1300°C in a constant flow of synthetic air (1.5 l/h). Based on the TGA curve, parts of the nanocomposite powder (~ 400 mg) were heated (1°C/min) in a tubular furnace in flowing air at selected temperatures between 250 and 1300°C. Immediately after the furnace has reached the desired temperature, the powders were quenched in air. The oxidized powders are hereafter named as C followed by the respective temperature of oxidation (for instance sample C250 is a powder heated at 250°C).

XRD patterns were recorded in the range 10-70° (2\( \theta \)) using a Bruker D4 Endeavor diffractometer equipped with a Cu K\(_\alpha\) radiation tube. Counts were registered every 0.02° (2\( \theta \)). The carbon content \( (C_n) \) was measured by the flash
combustion method (the accuracy of the measurements is ± 2 %). The powders were observed by FEG-SEM (JEOL JSM 6700F), with an acceleration tension of 5 kV using the in-lens electron detector. All powders were studied by transmission Mössbauer spectroscopy (TMS), integral low-energy electron Mössbauer spectroscopy (ILEEMS) and in-situ high-temperature transmission Mössbauer spectroscopy (HTTMS). TMS is used to study the bulk of the material while ILEEMS is applied to examine the surface of the powders. HTTMS spectra were recorded to obtain in-situ information about the oxidation processes of the CNT nanocomposite powder and to identify and quantify the oxidation products formed. At room temperature (25°C) both TMS and ILEEMS were employed. HTTMS was applied at selected temperatures between 25 and 850°C. The spectrometers were operating at constant acceleration mode with triangular reference signals. $^{57}$Co(Rh) sources were used. Isomer shifts are referenced with respect to $\alpha$-Fe at room temperature. ILEEMS is a variant of conventional TMS in which low-energy electrons are counted. The majority of these electrons, with energy of ~10 eV, are produced by after effects following the decay of the probe nuclei in an extremely thin surface layer of the absorber. Consequently, by comparing the ILEEMS results with those of TMS, information of the surface of the material can be inferred [9]. The HTTMS measurements were performed using a furnace made by Wissel Scientific Instruments (model MBF-1100). Two pipe connections were used to maintain in the sample chamber a gas flow of either synthetic air or N$_2$. The furnace was heated at 1°C/min under flow of synthetic air. After the furnace had reached the desired temperature the gas flow was switched to N$_2$ to avoid further oxidation of the powder. The N$_2$ flow was kept during the acquisition of the spectrum. With the spectrum containing enough statistics the flow was switched back to synthetic air and the temperature was increased at 1 °C/min up to the next desired temperature. The gas flow was then switched back to N$_2$ in order to collect the next spectrum. These steps were done consecutively until the furnace reached the maximum desired temperature (850 °C). Immediately after having recorded the spectrum at 850 °C, the flow of N$_2$ was switched to air and the furnace was cooled down to room temperature at natural cooling of the furnace. Subsequently a final spectrum was collected at 25°C.

3 RESULTS AND DISCUSSION

The TGA curve and the corresponding derivative curve (DTG) (Fig. 2) show several steps, involving both weight losses and gains at different stages. The initial weight loss at temperatures below 150°C is attributed to desorption, mostly corresponding to species adsorbed onto the surface of the CNTs. A weight gain is observed in the range 150-300°C. According to earlier studies [10], this weight gain could correspond to the oxidation of the Fe and Fe-carbide particles located at the surface and in the open porosity of the alumina grains. A second weight loss (-0.92%) is observed in the range 300-540°C. This weight loss is supposed [1] to be due to the oxidation of carbon, free or combined with iron. The DTG curve suggests that this process actually proceeds in two steps, which could indeed indicate the successive oxidation of different forms of carbon. However, the two steps are ill-resolved and sound conclusions in that respect cannot be drawn. Interestingly, Mössbauer spectroscopy results (see later in this section) indicate
that γ-Fe-C particles have not been oxidized at these temperatures. At temperatures increasing beyond 540°C, two successive weight gains are observed (DTG peaks at 670 and 1120°C). From earlier results on carbon-free metal-oxide powders [10,11], both weight gains are proposed to correspond to the oxidation of intragranular α-Fe particles. However, Mössbauer spectroscopy results (see later in this section) could indicate that the 1120°C peak also involve γ-Fe-C particles and a FeAl₂O₄ phase.

Fig. 2. TGA (a) and DTG (b) curves for the CNT-Fe-Al₂O₃ nanocomposite powder.

On the basis on the TGA curve discussed above, batches of the CNT-Fe-Al₂O₃ nanocomposite powder were calcined in air at 250, 300, 420, 540, 670, 850, and 1300°C. The carbon content Cₙ was found to gradually decrease from 1.6 to 0.2 wt.%) as the calcination temperature is increased to 850°C (Fig. 3). For C1300, Cₙ is below 0.2 wt.%, which is within the detection limit of the technique. A comparison can be made between the second weight loss measured in the TGA (-0.92 %) and that corresponding to the change in carbon content from room temperature to 540°C (-1.35%), the latter being significantly higher. This shows that the first weight gain and the second weight loss are superimposed and thus, it is not possible to extract from the TGA curve quantitative results neither for determining the contents of different carbon forms nor for assessing the oxidation yield of iron species in this temperature range (about 200-540°C).

Fig. 3. Carbon content versus the increase in calcination temperature.

Analyses of the XRD patterns for C0-C540 (Fig. 4) reveal the presence of α-Fe and/or Fe₃C (cementite) besides the α-alumina matrix. It is, however, difficult to discriminate between the patterns of α-Fe and Fe₃C because the respective diffraction peaks are strongly overlapping. α-Fe may also be present in the powders, but it cannot be resolved from the XRD patterns because its main (111) diffraction peak (d₁₁₁ = 0.208 nm) is probably masked by the α-alumina peak (d₁₁₃ = 0.209 nm). The intensity of the α-Fe and Fe₃C peaks regularly decreases upon the increase in calcination temperature above 540°C (C670 and C850). These peaks are no longer detected for C1300. From C300 to C850, hematite (α-Fe₂O₃) peaks are detected with increasing intensity. For C1300, the hematite peaks appear to be slightly less intense than for C850, which could indicate a partial dissolution into alumina.
Fig. 4. XRD patterns of the calcined powders. A: α-Al₂O₃ and H: α-Fe₂O₃.

Typical FEG-SEM micrographs for selected powders are shown in Fig.5.

Fig. 5. Typical FEG-SEM images of the calcined powders: a) C0; b) C300; c) C420; d) C540; e) C670; f) C1300.

It is difficult from such images to distinguish C0 (Fig. 5a), C250 (not shown), C300 (Fig. 5b) and C420 (Fig. 5c) from each other. Indeed, CNTs, CNT bundles and 15-30 nm nanoparticles located at the surface at the alumina grains are observed. By contrast, much less CNTs and CNT bundles are observed for C540 (Fig. 5d) and C670 (Fig. 5e). Moreover, for C670, a high density of nanoparticles with a uniform diameter (~20 nm) is observed. For C850 (not shown), CNTs are extremely rarely observed and for C1300 (Fig. 5f), no CNTs are observed. Interestingly, for C1300, no surface nanoparticles are observed. This could support the XRD result that hematite particles are dissolved into alumina after the treatment in air at 1300°C.

The TMS recorded at 25°C for all powders are reproduced in Fig. 6. Each spectrum in general was fitted as a superposition of different subspectra: an outer sextet due to α-Fe₂O₃, a middle sextet accounting for α-Fe, an inner sextet representing Fe₃C, a singlet characteristic of γ-Fe-C, an Fe³⁺ doublet ascribed to iron ions in the structure of α-Al₂O₃ (noted as (Al,Fe)₂O₃) and an Fe²⁺ doublet that reflects the presence of small amount of hercynite (FeAl₂O₄). Note that the α-Fe₂O₃ sextet was not present for C0. For C670 and C850, no Fe₃C component was resolvable, and for C1300 only the α-Fe₂O₃ sextet and the ferric doublet were found to exist. Consistently, the most adequate fits of the TMS were obtained assuming hyperfine parameter distributions for all components, hereby imposing a 3:2:1 ratio for the relative spectral areas of outer lines to middle lines to inner lines for the elemental sextets. The respective Mössbauer parameter values obtained from the data reductions are listed in Table 1. The presence of both the Fe³⁺ and Fe²⁺ doublets for C0 are due to the incomplete reduction of the solid solution. The remaining Fe³⁺ ions are deep within the alumina grains and it is possible that the Fe²⁺ ions correspond to a very thin (<5 nm) layer of FeAl₂O₄ surrounding some intragranular Fe nanoparticles, which has been observed before [12]. Note that the proportion of Fe²⁺ ions is not affected by heating at temperatures as high as 850°C (Table 1), which support the hypothesis that the corresponding species are within the
alumina grains. The relative spectral area (RA) of the hematite component gradually increases from 0 % (C0) to 32 % (C850), but exhibits a sudden drop to 19% for C1300. This indicates that the hematite particles have been partly dissolved into alumina in agreement with the above XRD and FEG-SEM results. The α-Fe contribution gradually decreases from 30 % (C0) to 12 % (C850), traducing the oxidation of the surface α-Fe particles, as opposed to the intragranular ones, and thus partly accounting for the increase of the hematite proportion. As mentioned above, no α-Fe is detected for C1300, the intragranular α-Fe particles having been oxidized too. A gradual decrease of the Fe3C proportion upon raising the calcination temperature is observed, from 21% (C0) to 6% (C540). For C670 onwards, no Fe3C is detected. Considering the respective proportion of α-Fe, Fe3C and α-Fe2O3 (Table 1), it appears clearly that both α-Fe and Fe3C are gradually oxidized into α-Fe2O3 as the calcination temperature is increased to 850°C. By contrast, and surprisingly, the proportion of γ-Fe-C is not affected by heating at temperatures as high as 850°C (Table 1). Kim and Sigmund [13] reported on large γ-Fe particles (100 nm in diameter) tightly encapsulated by a graphitic film. These authors inferred that the graphitic film prevents the γ-Fe from transforming into α-Fe (the stable phase of iron at room temperature). The study of the present powder by high-resolution transmission electron microscopy revealed the presence of encapsulated particles with diameters of 15 to 20 nm [8], which were too large for being active for the formation of CNTs and ended up covered by several graphene layers. Therefore, it is not unreasonable to propose that these are the γ-Fe-C particles and that after the oxidation of the graphene layers covering them, a very thin layer of α-Fe2O3 is formed at their surface, thus preventing a complete oxidation until high temperatures such as 850 °C while helping to retain the face-centered cubic structure. It is well-know that iron particles actively react with oxygen even at room temperature, resulting in an iron oxide layer on the surface of the particles protecting them from further inward oxidation. If this suggestion is indeed reasonable one would then wonder why no change in the area ratio was observed for the γ-Fe-C component (Table 1). The layer of hematite that could be covering the γ-Fe-C particles could be extremely thin so that the measurable abundance is within the experimental error and consequently one cannot observe changes in area ratio in the TMS. Indeed, De Grave et al. [9] observed by ILEEMS that very thin layers of α-Fe2O3 on Fe-containing particles are not detected by TMS.

![Fig. 6. TMS spectra (collected at 25 °C) of the calcined powder.](image-url)
Table 1. Relevant hyperfine parameters for the components present on the TMS spectra acquired at 25 °C for the CNT -Fe-Al₂O₃ nanocomposite powder heated in air at selected temperatures.

<table>
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<tr>
<th>Sample</th>
<th>$(\text{Al,Fe)}_2\text{O}_3$</th>
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<tr>
<td></td>
<td>$\Delta E_Q$</td>
<td>$\delta$</td>
<td>RA</td>
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<tr>
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<td>0.30</td>
<td>20</td>
</tr>
<tr>
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<td>23</td>
</tr>
<tr>
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<td>24</td>
</tr>
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<td>24</td>
</tr>
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<td>0.31</td>
<td>23</td>
</tr>
<tr>
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<td>25</td>
</tr>
<tr>
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<table>
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<th>$\gamma$-Fe-C</th>
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<td>25</td>
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<tr>
<td>C420</td>
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<td>25</td>
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<tr>
<td>C540</td>
<td>32.8</td>
<td>0.00</td>
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<tr>
<td>C1300</td>
<td>-</td>
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</table>

$B_{hf}$: hyperfine field at maximum of the distribution (T); $2\epsilon_Q$: quadrupole shifts (mm/s); $\Delta E_Q$: quadrupole splitting (mm/s); $\delta$: isomer shifts (mm/s); RA: relative spectral areas (%). The values of isomer shifts are with reference to metallic iron. * Fixed parameters.
ILEEMS experiments at 25°C were carried out to examine whether the surface of the powder is affected differently by the heating as compared to the bulk. The emission spectra (not shown) clearly exhibit the same shapes and in general the same spectral components as do the corresponding TMS spectra. This indicates that the different iron species are distributed evenly in the bulk and the top most surface of the grains. However, the relative area parameter RA for the hematite component in the ILEEMS spectrum of C250 is significantly higher than the corresponding value for the TMS spectrum (13% versus 6%, respectively). Concurrently the contribution of the α-Fe component has dropped to 19% from 27%. This finding suggests that the initial weight gain (250-300°C) observed in the TGA curve is due to oxidation of the topmost (5 nm) surface α-Fe particles. More details on ILEEMS studies on similar powders can be found elsewhere [14]. The differences between the present results and those of the earlier ILEEMS study arise because of the different oxidation conditions applied: quenching the powder in air immediately after reaching the maximum desired temperature (present study) or oxidation in air at 600 °C during 2 h [14].

The in-situ HTTMS spectra of the CNT-Fe-Al2O3 nanocomposite powder are reproduced in Fig. 7. Only three or four components were required to fit these spectra adequately: an α-Fe sextet, an (Al,Fe)2O3 doublet and a γ-Fe-C singlet, as well as, for the spectra collected at 250 and 300°C, an Fe3C sextet. The adjusted hyperfine parameter values are listed in Table 2 and are all in line with the corresponding values obtained from the TMS and ILEEMS experiments as described in the preceding sections. Some interesting features emerge from the HTTMS experiments:

(i) the absence of the hematite component in all HTTMS spectra while this component is prominently present in the spectrum recorded for the powder cooled down to room temperature after termination of the 850°C run;
(ii) the gradual increase of the contribution of the (Al,Fe)2O3 doublet up to 59 % while at the final run at 25°C only 31% is found, which is close to the value for the parent CNT-Fe-Al2O3, nanocomposite powder (CO);
(iii) the vanishing of the Fe3C subspectrum between 300 and 420°C while according to the TMS results this phase is still present after heating at 540°C;
(iv) up to 670°C, the contribution of α-Fe sextet remains unchanged within experimental error limits, whereas at 850 °C this contribution has decreased from 30 % to 21 %;
(v) the absence of the FeAl2O4 phase in all of the HTTMS spectra.

To comment on observations (i) to (v), the authors have collected some relevant RA data in Table 3. They concern on the one hand the percentage of the cementite component, RA_c, and the sum RA_ha of the hematite and alumina contributions both as obtained from the 25°C TMS (data from Table 1).
Table 2. Relevant hyperfine parameters for the components observed on the HTTMS spectra acquired at selected temperatures for the CNT-Fe-Al₂O₃ nanocomposite powder.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(Al,Fe)₂O₃</th>
<th>α-Fe₂O₃</th>
<th>Fe²⁺ doublet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔEₕ</td>
<td>δ</td>
<td>RA</td>
</tr>
<tr>
<td>250</td>
<td>0.52</td>
<td>0.25</td>
<td>27</td>
</tr>
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<td>300</td>
<td>0.54</td>
<td>0.21</td>
<td>32</td>
</tr>
<tr>
<td>420</td>
<td>0.55</td>
<td>0.14</td>
<td>50</td>
</tr>
<tr>
<td>540</td>
<td>0.60</td>
<td>0.10</td>
<td>50</td>
</tr>
<tr>
<td>670</td>
<td>0.61</td>
<td>0.01</td>
<td>50</td>
</tr>
<tr>
<td>850</td>
<td>0.56</td>
<td>-0.04</td>
<td>59</td>
</tr>
<tr>
<td>25</td>
<td>0.57</td>
<td>0.31</td>
<td>31</td>
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</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>α-Fe</th>
<th>Fe₃C</th>
<th>γ-Fe-C</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Bₕhf</td>
<td>δ</td>
<td>RA</td>
</tr>
<tr>
<td>250</td>
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<tr>
<td>540</td>
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<tr>
<td>670</td>
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<td>-0.27</td>
<td>30</td>
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<tr>
<td>850</td>
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<td>25</td>
<td>32.4</td>
<td>0.00</td>
<td>10</td>
</tr>
</tbody>
</table>

Bₕhf: hyperfine field at maximum of the distribution (T); 2ε₀: quadrupole shifts (mm/s); ΔEₕ: quadrupole splitting (mm/s); δ: isomer shifts (mm/s); RA: relative spectral areas (%). The values of isomer shifts are with reference to metallic iron. * Fixed parameters.
On the other hand, the right part of Table 3 contains the RA values of the cementite and alumina phases, \( R_{A_c} \) and \( R_{A_a} \) respectively, calculated from the in-situ HTTMS (data from Table 2). The sum \( R_{A_c} + R_{A_{ha}} \) remains constant at \( \sim 50\% \), except for the highest temperature of 850°C at which \( R_{A_c} + R_{A_{ha}} \) has increased to 61\%. For this latter temperature, the \( \alpha \)-Fe contribution has dropped to 21\% from the otherwise constant value of \( \sim 30\% \) found for the lower temperatures (Table 2). This indicates that part of the \( \alpha \)-Fe particles has oxidized, presumably forming \( \alpha \text{-Fe}_2\text{O}_3 \). Hematite is paramagnetic at high temperatures (\( T > 668°C \)) and hence gives rise to a doublet with hyperfine parameters that are very similar to those of the present (Al,Fe)\(_2\)O\(_3\) doublet [15]. As a consequence, the hematite doublet is obscured by and cannot be distinguished from the alumina doublet. This feature explains the concomitant changes in the RA values for the \( \alpha \)-Fe sextet and the ferric doublet assigned to (Al,Fe)\(_2\)O\(_3\) upon increasing the measuring temperature from 670 to 850°C. Based on the well-known Néel-Brown expression for the superparamagnetic relaxation time the size of the hematite particles is estimated to be around 25 nm.

The data of Table 3 indicate that the oxidation of Fe\(_3\)C gives rise to \( \alpha \text{-Fe}_2\text{O}_3 \), as could be expected. The reason that no hematite sextet is observed in the HTTMS for temperatures \( T \geq 250°C \) is believed to be the small size of the hematite particles and, as a consequence thereof, their superparamagnetic behaviour at temperatures exceeding some so-called blocking temperature. Evidence for the small particle size is provided by the low value of the magnetic hyperfine field for the hematite sextets in the room-temperature TMS spectra of the heated powders (Table 1 - \( B_{hf} \) for bulk hematite is 51.7 T). When the temperature of the absorber is increased to a value higher than this blocking temperature, the Mössbauer event experiences a zero hyperfine field and the resulting spectrum has collapsed to a doublet with quadrupole splitting equal to the value corresponding to the paramagnetic state, i.e., a doublet which remains unresolved from the (Al,Fe)\(_2\)O\(_3\) doublet. According to the results of Bødker and Mørup [16] \( \alpha \text{-Fe}_2\text{O}_3 \) particles with average particle size of 27 nm, which is about the size of the particles expected for the presently involved hematite phase, have a median blocking temperature of 70°C. Such particles, if their size were rather uniform, which can be expected in the present case, would thus give rise to a well-defined sextet at 25°C and a doublet at 250°C or higher.

### Table 3. Some relevant relative spectral areas (in % of total spectrum area) obtained from the transmission Mössbauer spectra (TMS) collected at 25 °C for the CNT-Fe-Al\(_2\)O\(_3\) nanocomposite powder after calcination in air at temperatures \( T_c \) and as obtained from in-situ high-temperature transmission Mössbauer spectra (HTTMS) collected at temperatures \( T \) of the CNT-Fe-Al\(_2\)O\(_3\) nanocomposite powder. Estimated errors are ±2%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TMS ( R_{A_c} )</th>
<th>TMS ( R_{A_{ha}} )</th>
<th>HTTMS ( R_{A_c} )</th>
<th>HTTMS ( R_{A_{ha}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0(^\circ)</td>
<td>20</td>
<td>21</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>C250</td>
<td>29</td>
<td>16</td>
<td>250</td>
<td>27</td>
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<td>C300</td>
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<td>C420</td>
<td>41</td>
<td>7</td>
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<td>50</td>
</tr>
<tr>
<td>C540</td>
<td>43</td>
<td>6</td>
<td>540</td>
<td>50</td>
</tr>
<tr>
<td>C670</td>
<td>51</td>
<td>-</td>
<td>670</td>
<td>50</td>
</tr>
<tr>
<td>C850</td>
<td>61</td>
<td>-</td>
<td>850</td>
<td>59</td>
</tr>
</tbody>
</table>

\( ^\circ \)sum for hematite and alumina component
\( ^\circ \)cementite component
\( ^\circ \)alumina component
\( ^\circ \)results for parent non-calcined powder

The absence of the Fe\(^{2+}\) due to FeAl\(_2\)O\(_4\) phase in all of the HTTMS spectra is believed to be due to the weak contribution of this component (5 % for sample C0, Table 1), which is then
overlapped by the other components in the central part of the spectra.

After acquisition of the HTTMS at 850°C and subsequent cooling down the sample to room temperature in air, its spectrum was again measured in TMS (Fig. 8a). The hyperfine parameters of the various components that could be resolved from that spectrum (Table 2) were found to be very similar to those obtained from the TMS for C850 (Table 1). An ILEEMS measurement at 25°C for the powder resulting from HTTMS measurements was performed (Fig. 8b).

The emission spectrum has the same shape and spectral components as does the HTTMS spectrum at 25°C (Fig. 8a). The contributions of all components, i.e., hematite, α-Fe, γ-Fe-C, Fe\(^{3+}\) doublet and Fe\(^{2+}\) doublet are, within experimental errors limits, the same for the respective HTTMS and ILEEMS spectra indicating that all Fe-containing phases are evenly distributed between the bulk and the outer porosity on the one hand and at the surface of the grains on the other hand. It should be mentioned that the hyperfine parameters of all components obtained from the ILEEMS are within error limits identical to the values fitted to the HTTMS spectrum at 25°C.

4. CONCLUSIONS

The thermal stability of a CNT-Fe-Al\(_2\)O\(_3\) nanocomposite powder was studied using notably TGA and Mössbauer spectroscopy. In particular, in-situ high-temperature transmission Mössbauer spectroscopy was performed for the first time on such materials. The oxidation process of the powder is characterized by several steps. The first weight gain (150-300°C) was attributed to the oxidation into hematite (α-Fe\(_2\)O\(_3\)) of the α-Fe and Fe-carbide particles located at the surface and in the open porosity of the alumina grains, whereas a weight loss (300-540°C) was thought to be the oxidation of carbon found as CNTs and graphene layers surrounding the Fe and Fe\(_3\)C particles. The formation of hematite was observed to start at about 250°C. It was demonstrated that the hematite particles are superparamagnetic at temperatures equal to 250°C or higher and were found to be approximately 25 nm in diameter. A remarkable aspect is that γ-Fe-C is unaffected even after oxidation at 850°C. It was suggested that the encapsulation of γ-Fe-C particles by graphene layers leads to the stability of these particles, i.e. retention of γ (face-centered cubic) structure and in addition prevents them from oxidation. With the increase in calcination temperature, the graphene layers are oxidized and a very thin layer of α-Fe\(_2\)O\(_3\) is formed at the surface of the γ-Fe-C particles, preventing the complete oxidation of the γ-Fe-C particles until at least 850°C, while
helping to retain the face-centered cubic structure. Finally, two successive weight gains at 670 and 1120°C could correspond to the oxidation of the intragranular $\alpha$-Fe particles and the $\gamma$-Fe-C particles.

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Surface composition of carbon nanotubes-Fe-alumina nanocomposite powders: an integral low-energy electron Mössbauer spectroscopic study

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Surface Composition of Carbon Nanotubes-Fe-Alumina Nanocomposite Powders: An Integral Low-Energy Electron Mössbauer Spectroscopic Study

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The surface state of carbon nanotubes-Fe-alumina nanocomposite powders was studied by transmission and integral low-energy electron Mössbauer spectroscopy. Several samples, prepared under reduction of the α-Al2O3-Fe3O4 precursor in a H2-CH4 atmosphere applying the same heating and cooling rate and changing only the maximum temperature (800–1070 °C) were investigated, demonstrating that integral low-energy electron Mössbauer spectroscopy is a promising tool complementing transmission Mössbauer spectroscopy for the investigation of the location of the metal Fe and iron-carbide particles in the different carbon nanotubes-nanocomposite systems containing iron. The nature of the iron species (Fe²⁺, Fe³⁺, α-Fe, γ-Fe—C) is correlated to their location in the material. In particular, much information was derived for the powders prepared by using a moderate reduction temperature (800, 850, and 910 °C), for which the transmission and integral low-energy electron Mössbauer spectra are markedly different. Indeed, α-Fe and Fe²⁺ were not observed as surface species, while γ-Fe—C is present at the surface and in the bulk in the same proportion independent of the temperature of preparation. This could show that most of the nanoparticules (detected as Fe³⁺) and/or γ-Fe—C that contribute to the formation of carbon nanotubes are located in the outer porosity of the material, as opposed to the topmost (ca. 5 nm) surface. For the higher reduction temperatures, T, of 990 °C and 1070 °C, all Fe and Fe-carbide particles formed during the reduction are distributed evenly in the bulk and the surface of the matrix grains. The integral low-energy electron Mössbauer spectroscopic study of a powder oxidized in air at 600 °C suggests that all Fe³⁺ particles oxidize to α-Fe₂O₃, while the α-Fe and/or γ-Fe—C are partly transformed to Fe₃O₄ and α-Fe₂O₃, the latter phase forming a protecting layer that prevents total oxidation.

Introduction

Since their discovery by Iijima,1 carbon nanotubes have been one of the most actively studied materials in nowadays’ research. In a recent listing of most popular subjects in physics research,2 carbon nanotubes are first. This widespread interest is explained by the potential extraordinary technological applications of this material. Among the many possible application fields are ceramic/matrix nanocomposites containing carbon nanotubes.3 One of the main hurdles for the successful preparation of such composites is to obtain a homogeneous distribution of undamaged carbon nanotubes into the matrix. To overcome the need for a mechanical-mixing step during powder preparation, a direct method for the in situ synthesis of the carbon nanotube into an Al₂O₃ matrix has been proposed.4 It is based on a catalytic chemical vapor deposition route involving the reduction in H₂—CH₄ gas atmosphere of alumina-hematite solid solutions, producing carbon nanotubes-Fe—Al₂O₃ nanocomposite powders. The reduction first produces nanometric Fe particles that are active for the decomposition of CH₄ and subsequently for the formation of carbon nanotubes if their diameter is small enough (< ca. 5 nm).5,6

It is well-known that 57Fe Mössbauer spectroscopy offers several advantages for studies of iron-containing compounds. The spectra and parameters derived from these are very sensitive to electronic, magnetic, and structural characteristics of the probed material, and as such, Mössbauer spectroscopy is a useful tool for phase identification and quantification of mixtures of Fe-bearing solid materials. Although Fe species are often involved in carbon nanotube formation processes, only relatively few carbon nanotube-related studies, apart from those by some of the present authors,7—10 report on Mössbauer data with regard to the formation, evolution, and the spatial distribution of Fe-containing particles after synthesis of the carbon nanotubes by catalytic chemical vapor deposition methods.11—19 Furthermore, some authors reported on the characterization by Mössbauer spectroscopy of metal-filled carbon nanotubes.20—27 Finally, Mössbauer spectroscopy was applied in the characterization of carbon nanotubes decorated with iron oxides.28,29

In a previous work,6 carbon nanotubes-Fe—Al₂O₃ nanocomposite powders were prepared by the H₂—CH₄ reduction of α-Al₂O₃-Fe₃O₄ at different temperatures. The carbon nanotubes were mostly single and double walled, but thicker carbon nanofibers were also observed. By using several characterization techniques including conventional transmission Mössbauer spectroscopy, several iron species were detected in the nanocomposite powders: Fe¹⁷ ions still present in the α-alumina lattice, α-Fe, γ-Fe—C, and cementite (Fe₃C). Three major


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conclusions were inferred: (i) the γ-Fe–C particles are embedded inside the matrix grains, (ii) the cementite particles are on the surface of the matrix grains, and (iii) the α-Fe particles are found both inside and on the surfaces of the grains. It was further proposed that the nanoparticles responsible for the formation of carbon nanotubes ended up as FeC after cooling down from the selected temperature ($T_r$).

In the present work, the authors for the first time have studied the surface of these powders by integral low-energy electron Mössbauer spectroscopy. This technique is a variant of transmission Mössbauer spectroscopy in which low-energy electrons are counted. These electrons, with energy of ~10 eV, are produced by after effects following the decay of the probe nuclei in the absorber. As a consequence of this low energy, only an extremely thin surface layer (about 5 nm) of the material is probed.

It was the intention using this unique technique to obtain further and more accurate information on the spatial distribution of the Fe-bearing particles with respect to the nano composite grains.

Experimental Section

The synthesis of the powders and their characterization by X-ray diffraction, carbon element analysis, specific surface area measurements, and transmission and scanning electron microscopy are described in detail elsewhere. Briefly, the carbon nanotube-Fe-Al2O3 nanocomposite powders were prepared by the reduction of α-Al2O3Fe2O3 in H2–CH4 (18 mol % CH4) at different temperatures ($T_r$: 800, 850, 910, 990, and 1070 °C). The heating rate to $T_r$ and the subsequent cooling rate were equal to 10 °C/min, and no dwell time was applied at $T_r$. The so-obtained nanocomposite powders are designated in the following as R800, R850, R910, R990, and R1070, according to the corresponding $T_r$.

The powders were observed by field-emission gun-scanning electron microscopy. Mössbauer spectra at room temperature were collected with spectrometer operating in constant acceleration mode with triangular reference signal. 57Co(Rh) sources were used. Both conventional transmission spectra and integral low-energy electron Mössbauer spectra (hereafter referred as emission spectra) have been acquired. All Mössbauer spectra were computer-analyzed in terms of model-dependent distributions of hyperfine-parameter values and numerical data quoted hereafter refer to maximum-probability values. Isomer shifts are referenced with respect to α-Fe at room temperature.

The fine width values were adjusted in the transmission spectra (Table 1) do not significantly differ from the respective values derived from the transmission spectra. For R990 and R1070, all four iron phases are recognized, however, with slightly different relative spectral areas from those observed in the transmission spectra (Table 1), showing that all species are present in the topmost surface of the grains. Interestingly, the emission spectra of samples R800, R850, and R910 do not show spectral components due to α-Fe and FeC, suggesting that the involved particles are not located at the topmost surface of the alumina grains. The relative spectral area contributions of the γ-Fe–C sub-spectra to the total spectra are found to be the same in the respective transmission and emission experiments, suggesting that γ-Fe–C particles are evenly distributed between the surface and those deeper in the material. The absence of α-Fe and FeC components in the emission spectra is totally accounted for by the more intense Fe3+ doublet in the latter spectra as witnessed by the respective relative spectral area values. These results, in particular, the absence of FeC in the topmost layer, are puzzling because they are partly in contradiction with the earlier conclusions mentioned above.

![Figure 1](image1.png)

Figure 1. Transmission (left) and emission (right) spectra of the nanocomposites powders measured at room temperature, α-Fe (red), FeC (blue), (αFe2O3) (olive), γ-Fe–C (cyan).

Results and Discussion

The transmission spectra of the nanocomposite powders are shown in Figure 1 (left) and the corresponding Mössbauer parameters are summarized in Table 1. All spectra have been analyzed with superpositions of model-independent hyperfine-field and quadrupole-splitting distributions. Four components were found to be required to obtain adequate fits for these spectra: (i) an outer sextet showing hyperfine parameters that are characteristic of α-Fe, (ii) an inner sextet that could be attributed to FeC, (iii) an Fe3+ doublet due to iron ions present in the lattice of the α-alumina, and (iv) a singlet that corresponds to a γ-Fe phase, possibly alloyed with carbon (γ-Fe–C). No significant differences in parameter values between the presently measured transmission data and those obtained earlier were observed. Obviously, increasing the temperature of reduction has a major influence on the transmission spectra, in particular, as to the contribution of the central doublet (accounting for Fe2+ ions) which decreases considerably with increasing $T_r$ (Figure 1 top and Table 1). This decrease is accounted for by the gradual increase of the other components present in the transmission spectra.

The results of the integral low-energy electron Mössbauer spectroscopic experiments are shown in the right panel of Figure 1. The emission spectra exhibit the same shape as the transmission spectra (Figure 1, left). The fitted hyperfine parameters (Table 1) do not significantly differ from the respective values derived from the transmission spectra. For R990 and R1070, all four iron phases are recognized, however, with slightly different relative spectral areas from those observed in the transmission spectra (Table 1), showing that all species are present in the topmost surface of the grains. Interestingly, the emission spectra of samples R800, R850, and R910 do not show spectral components due to α-Fe and FeC, suggesting that the involved particles are not located at the topmost surface of the alumina grains. The relative spectral area contributions of the γ-Fe–C sub-spectra to the total spectra are found to be the same in the respective transmission and emission experiments, suggesting that γ-Fe–C particles are evenly distributed between the surface and those deeper in the material. The absence of α-Fe and FeC components in the emission spectra is totally accounted for by the more intense Fe3+ doublet in the latter spectra as witnessed by the respective relative spectral area values. These results, in particular, the absence of FeC in the topmost layer, are puzzling because they are partly in contradiction with the earlier conclusions mentioned above.

Field-emission gun-scanning electron microscopy images of selected composite powders are reported in Figure 3. For R800
TABLE 1: Mößbauer Results of the Carbon Nanotubes-Fe Alumina Nanocomposite Samples Measured at Room Temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>$H_{iso}$</th>
<th>$2\Delta$</th>
<th>$N_A$</th>
<th>$\delta$</th>
<th>$H_{iso}$</th>
<th>$2\Delta$</th>
<th>$N_A$</th>
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<td>24</td>
<td>0.14</td>
<td>84</td>
<td>0.03*</td>
<td>17</td>
</tr>
</tbody>
</table>

Integral Low-Energy Electron Mößbauer Spectroscopy

$H_{iso}$: hyperfine field at maximum of the distribution (T), $2\Delta$: quadrupole shifts (mm/s), $N_A$: quadrupole splitting (mm/s), $\delta$: isomer shifts (mm/s), $R_A$: relative spectral area (%). The values of isomer shifts are with reference to metallic iron. *Fixed parameters.

C. These particles are fairly large, contrary to a previous hypothesis that the $gamma$ phase, as opposed to the $alpha$ phase, was an indication of a very low size. Because there is an increase in the content of carbon nanotubes between R800 and R850 but no marked increase in the $gamma$-Fe-C proportion (Table 1), one could propose that most of the nanoparticles (detected as Fe-C and Fe$_4$C) that contribute to the formation of carbon nanotubes are located in the outer porosity of the material, as opposed to the surface. Particles located in a pore would be less prone to excessive growth than a surface particle would. This in line with earlier results showing that the diameter of the surface particles (about 10–20 nm) is far too high for them to be active for the formation of carbon nanotubes. Indeed, the critical diameter is in the range 1–5 nm, and larger particles either become totally covered by carbon layers or are active for the formation of carbon nanofibers.

In order to gather more information about the location of the different iron phases in the nanocomposite powders, that is, inside the matrix grains, the outer porosity, or on their surfaces, sample R950 was heat-treated in air at 600 °C for 2 h and studied by transmission Mößbauer spectroscopy. Note that this treatment burns all of the carbon nanotubes and carbon nanofibers. The transmission and the emission spectra were collected at room temperature for this sample designated R950x500 in the following (Figure 4). The hyperfine parameters obtained from the fit of the spectra are listed in Table 2. In contrast to the transmission, the emission spectrum is composed of only four components (instead of five) which are: (i) a sextet with hyperfine parameters characteristic of hematite (Fe$_3$O$_4$); (ii) a doublet due to $gamma$-Fe-C; (iii) an Fe$_4$C doublet; and (iv) a second broad and less intense doublet that resembles the doublet in the aforementioned transmission spectrum and which has been suggested to arise from an Fe$_4$Al$_2$O$_4$ phase. The (α-alumina) Fe$^{3+}$, the (α-Fe$_3$O$_4$), and the $gamma$-Fe-C components represent similar contributions in both the transmission and the emission spectra, while the broad doublet component is considerably more abundant in the emission spectrum (Table 2). The transmission spectrum showed, in addition to the phases mentioned above, a contribution due to α-Fe particles (relative spectral area ~8%; see Table 2). Interestingly, cementite is not detected in the transmission nor in the emission spectrum, showing that these particles have entirely been oxidized and that they were easily accessible to the oxidizing atmosphere, whether they were located in the outer porosity or on the surface of the alumina grains. The Fe$^{3+}$ doublet represents the iron ions that were still present in the lattice of α-alumina after...
Figure 3. Field-emission gun-scanning electron microscopy images of nanocomposite powders: R800 (a), R850 (b), R910 (c), and R950 (d). CNTs, carbon nanotubes; and CNFs, carbon nanofibers.

Figure 4. Transmission (top) and emission (bottom) spectra collected at room temperature of sample R950 oxidized at 600 °C in air. α-Fe₂O₃ (blue); γ-Fe₂O₃ (red); (Al₂Fe₆)O₁₀ (olive); γ-Fe(C) (cyan); doublet (dark yellow).

The reduction step (i.e., for specimen R950), which of course are not affected by the oxidation in air. Comparing the relative contributions (spectral area; Table 2) could indicate that the hematite particles are formed by the oxidation of cementite. This is consistent with the findings reported by Dong et al. on the basis of thermal analysis of synthetic cements.

No α-Fe is detected in the emision spectrum, which could indicate that most α-Fe particles remaining in the R950 and 600 specimens are in intragranular position. This is in agreement with previous findings showing that intragranular metal particles in similar carbon-free metal-Al₂O₃ powders do not oxidize in flowing air below about 800 °C. The surface α-Fe particles were thus oxidized into species that could contribute to the broad doublet component. It could also be proposed that the γ-Fe-C particles that did not oxidize (about 70% of the population) were the larger ones and/or those covered by many carbon layers, whereas those that were less protected oxidized into species that could contribute to the broad doublet component. With regard to the formation of the Fe₃Al₂O₄ phase, it implies that α-Fe and γ-Fe-C particles would have reacted with the alumina matrix grains during the reduction step. However, one can argue that the broad doublet, suggested to be due to that phase, actually is representative for another Fe-containing oxide. The adjusted values for the quadrupole splittings and isomer shifts are indeed drastically deviating from those found for synthetic Fe₃Al₂O₄. Identification of the precise nature of the Fe phase on the basis of the adjusted doublet parameters is, however, not possible because of the strong overlap of the weak and broad doublet lines with the other absorption/emission lines present in the central part of the spectra and hence the ill-defined values of the hyperfine parameters of the doublet. It is not unreasonable that the doublet can be attributed to wustite, Fe₃O₄, that may indeed form under the conditions applied in the present oxidation experiments. It is well-known that iron particles in general actively react with oxygen even at room temperature, resulting in an iron oxide layer on the surface of the particles. The formation of these oxide layers can protect the particles against further inward oxidation. Fung et al. have reported the remarkable resistance against oxidation of passivated nanopar-
TABLE 2: Mössbauer Results at Room Temperature of Sample R990ox600*

<table>
<thead>
<tr>
<th></th>
<th>Transmission Mössbauer Spectroscopy</th>
<th>Integral Low-Energy Electron Mössbauer Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-FeO</td>
<td>α-Fe</td>
<td>(ALF)O</td>
</tr>
<tr>
<td>Hδm</td>
<td>2ε₀</td>
<td>RA</td>
</tr>
<tr>
<td>50.9</td>
<td>-0.19</td>
<td>30</td>
</tr>
<tr>
<td>51.0</td>
<td>-0.19</td>
<td>29</td>
</tr>
</tbody>
</table>

* Hδ, hyperfine field at maximum of the distribution (T); 2ε₀, quadrupole shift (mm/s); ΔE₀, quadrupole splitting (mm/s); δ, isomer shift (mm/s). RA, relative spectral area (%). The values of isomer shifts are with reference to metallic iron. *Fixed parameters.

Acknowledgment. This work was partially funded by the Fund for Scientific Research—Flanders, and by the Special Research Fund (BOF, Bijnuated Onderzoeksfonds), UGent (B/06633), Belgium.

References and Notes

Conclusions
The study of carbon nanotubes-Fe-alumina nanocomposite powders by integral low-energy electron Mössbauer spectroscopy has given detailed information about the surface state of the powders, demonstrating that this technique is a promising tool complementing transmission Mössbauer spectroscopy for the investigation of the location of the metal Fe and iron-carbide particles on different carbon nanotubes-nanocomposite systems containing iron. In particular, much information was derived for the powders prepared by using a moderate reduction temperature (800, 850, and 910 °C), for which the transmission and emission spectra are markedly different. Indeed, α-Fe and Fe₂C were not observed as surface species, while γ-Fe-C was present at the surface and in the bulk in the same proportion independent of the temperature of preparation. This could show that most of the nanoparticles (detected as Fe₃C and/or γ-Fe-C) that contribute to the formation of carbon nanotubes are located in the outer porosity of the material, as opposed to the surface. A location in a pore would prevent excessive growth more efficiently than a location on the surface. The integral low-energy electron Mössbauer spectroscopic study of a powder oxidized in air at 600 °C suggests that all Fe₂C particles oxidize to α-Fe₂O₃ while the α-Fe and γ-Fe-C are partially transformed to Fe₃O₄ and α-Fe₂O₃, the latter phase forming a protective layer that prevents total oxidation. Thus, some surface particles are not monophased after oxidation.
Carbon Nanotubes–Fe-Alumina Nanocomposites

Paper VI

Integral low-energy electron Mössbauer spectroscopic studies of the surfaces of carbon nanotube-nanocomposite powders

V.G. de Resende, E. De Grave, Ch. Laurent

Hyperfine Interact. (2009) accepted
(Peer reviewed conference proceedings)
Integral low-energy electron Mössbauer spectroscopic studies of the surfaces of carbon nanotube-nanocomposite powders

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Abstract
The surface state of CNTs-Fe-Al₂O₃ and CNTs-Fe-MgAl₂O₄ nanocomposite powders was studied by integral low-energy electron Mössbauer spectroscopy (ILEEMS). Several samples, prepared by reduction of α-(Al,Fe)₂O₃ or (Mg,Fe)Al₂O₄ precursors in a H₂-CH₄ atmosphere, were investigated, demonstrating that ILEEMS is a promising tool completing transmission Mössbauer spectroscopy for the investigation of the metal Fe and iron-carbide particles in the different carbon nanotube systems.

1 Introduction
Carbon nanotubes (CNTs) have been named as the king of nanotechnology due to their uniqueness and their surprising properties. In addition to their unparalleled microstructure, the CNTs have demonstrated to possess extremely useful structural, electrical, thermal, and chemical characteristics that enable to use them as constituents for the production of a variety of industrial substitutes that are lighter and yet stronger, cheaper, more efficient, and more precise in their function. Although Fe species are often involved in CNTs formation processes, only few studies have reported on Mössbauer data with regard to the surface composition of CNTs-nanocomposite powders. The present authors have successfully applied ILEEMS for the characterization of the surfaces of CNTs-nanocomposite powders [1]. ILEEMS is the acronym for Integral Low-energy Electron Mössbauer Spectroscopy. It is a variant of transmission Mössbauer spectroscopy in which low-energy electrons are counted. These electrons, with energy of ~10 eV, are produced by after effects following the decay of the probe nuclei in the absorber. As a consequence of this low energy, only an extremely thin surface layer (few nanometers) of the material is preferentially probed [2]. In this contribution ILEEMS results will be presented for different selected CNTs-nanocomposite systems. These nanocomposite systems were synthesized and characterized by several techniques earlier [3,4]. It is intended to demonstrate that the characteristics of the top surface layers of these systems are very often significantly different as compared to what is observed for the bulk by transmission Mössbauer spectroscopy.
2 Experimental

The synthesis of the CNTs-Fe-Al$_2$O$_3$ and CNTs-Fe-MgAl$_2$O$_4$ and their characterization by X-ray diffraction, transmission Mössbauer spectroscopy, transmission- and scanning electron microscopy are described in detail elsewhere [3,4]. Briefly, the CNTs-Fe-Al$_2$O$_3$ nanocomposite powders were prepared by a catalytic chemical vapor deposition (CCVD) route involving the reduction of $\alpha$-(Al$_{1-x}$Fe$_x$)$_2$O$_3$ ($x = 0.05, 0.07$ and $0.10$) oxides in H$_2$-CH$_4$ (20 mol.% CH$_4$) at 1025 °C. The resulting CNTs-Fe-Al$_2$O$_3$ nanocomposite powders are code named as PXR, where X stands for the Fe content in cat.% in the precursor oxide. On the other hand, the CNTs-Fe-MgAl$_2$O$_4$ nanocomposite powders were prepared by the reduction of Mg$_{1-y}$Fe$_y$Al$_2$O$_4$ ($y = 0.3$ and $0.4$) in H$_2$-CH$_4$ gas mixture (18 mol.% CH$_4$) for 6 min at 1070 °C. For the sake of brevity, the samples are referred to according to the following example: the sample Mg7Fe3R is nanocomposite powder prepared from the Mg$_{0.7}$Fe$_{0.3}$Al$_2$O$_4$ precursor powder.

Mössbauer spectra at room temperature were collected with a spectrometer operating in constant acceleration mode with triangular reference signal. $^{57}$Co(Rh) source was used. Isomer shifts are referenced with respect to $\alpha$-Fe at room temperature.

3 Results and discussion

CNTs-Fe-Al$_2$O$_3$ nanocomposite powders

The ILEEMS (emission spectra) of the nanocomposite powders are shown in Fig. 1 and the corresponding Mössbauer parameters are summarized in Table 1. The spectra have been analyzed with superpositions of model-independent hyperfine field and quadrupole-splitting distributions [5]. Four components were found to be required to obtain adequate fits for these spectra: (a) an outer sextet characteristic of $\alpha$-Fe, (b) an inner sextet that could be attributed to Fe$_3$C, (c) an Fe$^{3+}$ doublet due to iron ions present in the lattice of the $\alpha$-Al$_2$O$_3$, and (d) a singlet that corresponds to a $\gamma$-Fe phase, which may possibly be alloyed to carbon ($\gamma$-Fe-C).

Basically, the emission spectra exhibit the same shape as that of the transmission spectra as reported by de Resende et al. and also the hyperfine parameters (Table 1) do not significantly differ from those derived from the latter [3]. The relative spectral areas $RA$ of the respective Fe phases as obtained from the transmission and emission spectra are listed in Table 2. Although significant differences for some of these values are noticed, they do indicate that all four Fe species mentioned above are present in the topmost surface layers of the grains. Interestingly, the emission spectrum of sample P5R does not show an Fe$^{2+}$ doublet, suggesting that the involved phase has formed only inside the cores of the alumina grains. It is further noticed that the $RA$ values for the $\alpha$-Fe components are smaller for the emission spectra as
compared to those obtained from the transmission spectra, thus accounting for the more intense Fe$^{3+}$ doublet of the Fe-substituted α-alumina.

Table 1. ILEEMS results of the CNTs-Fe-Al$_2$O$_3$ nanocomposite samples measured at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$B_{hf,m}$</th>
<th>$2\delta_Q$</th>
<th>$\delta$</th>
<th>$B_{hf,m}$</th>
<th>$2\delta_Q$</th>
<th>$\delta$</th>
<th>$\Delta E_{Q,m}$</th>
<th>$\delta$</th>
<th>$\Delta E_Q$</th>
<th>$\delta$</th>
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<tbody>
<tr>
<td>P5R</td>
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<td>0.00*</td>
<td>20.8</td>
<td>0.03*</td>
<td>0.19*</td>
<td>0.57</td>
<td>0.32</td>
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</tr>
<tr>
<td>P7R</td>
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<td>20.3</td>
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<td>0.57</td>
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<td>-0.11</td>
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$B_{hf,m}$: hyperfine field at maximum of the distribution (T); $2\delta_Q$: quadrupole shifts (mm/s); $\Delta E_{Q,m}$: quadrupole splitting (mm/s); $\delta$: isomer shifts (mm/s). The values of isomer shifts are with reference to metallic iron. * Fixed parameters.

**Fig. 1** Transmission (left) and emission (right) spectra of the CNTs-Fe-Al$_2$O$_3$ nanocomposite powders measured at room temperature. α-Fe (black); Fe$_3$C (gray); (Al,Fe)$_2$O$_3$ (light gray); γ-Fe-C (dark gray); Fe$^{2+}$ doublet (white)
Table 2. Relative spectral areas (RA values) derived from the Mössbauer spectra (emission and transmission) of the CNTs-Fe\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} nanocomposite samples measured at room temperature. Results for transmission spectra are from Ref. [3].

<table>
<thead>
<tr>
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<td>14</td>
<td>20</td>
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<td>29</td>
<td>36</td>
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<tr>
<td>Fe\textsubscript{3}C</td>
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<td>16</td>
<td>20</td>
<td>22</td>
<td>24</td>
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<tr>
<td>(Al,Fe)\textsubscript{2}O\textsubscript{3}</td>
<td>38</td>
<td>33</td>
<td>35</td>
<td>26</td>
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<tr>
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<td>20</td>
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<tr>
<td>Fe\textsuperscript{2+} doublet</td>
<td>7</td>
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</tbody>
</table>

**CNTs-Fe-MgAl\textsubscript{2}O\textsubscript{4} nanocomposite powders**

The transmission spectra of the nanocomposite powders are shown in Fig. 2 (left panel) and the corresponding Mössbauer parameters are summarized in Table 3. All spectra have been analysed with superpositions of model-independent hyperfine-field and quadrupole-splitting distributions. Four components were used in the fits of the spectra: one doublet, two sextets and one singlet. No significant differences in parameter values between the presently measured transmission data and those obtained earlier by Coquay et al. [4] were observed. According to these authors, the doublet is attributable to Fe\textsuperscript{2+} substituting for Mg\textsuperscript{2+} in the spinel structure. The contribution of the doublet to the total spectra is very weak and therefore in the analyses of the present transmission spectra its hyperfine parameters were kept fixed at the values reported by Coquay et al. [4]. The outer sextet is due to α-Fe particles while the inner one is characteristic of Fe\textsubscript{3}C. Regarding the singlet, the negative value of its isomer shift at room temperature suggests a γ-Fe-C phase.

The results of the ILEEMS experiments are shown in the right panel of Fig. 2. The emission spectra exhibit the same shape as the transmission spectra. The adjusted hyperfine parameters (Table 3) do not differ from the respective values derived from the transmission experiments, however, differences in the contributions (RA values) of each of the subspectra can be noticed, except for the Fe\textsuperscript{2+} doublet (Table 4).
Fig. 2 Emission spectra of the CNTs-Fe-MgAl₂O₄ nanocomposite powders measured at room temperature. α-Fe (black); Fe₃C (gray); Fe²⁺ doublet (light gray); γ-Fe-C (dark gray)

Table 3. Mössbauer results of the CNTs-Fe-MgAl₂O₄ nanocomposite samples measured at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transmission spectra</th>
<th>Emission spectra</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>α-Fe</td>
<td>Fe₃C</td>
</tr>
<tr>
<td>Mg7Fe3R</td>
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</tr>
<tr>
<td>Mg6Fe4R</td>
<td>33.0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bₘ · m</th>
<th>2ᵦ₀</th>
<th>δ</th>
<th>Bₘ · m</th>
<th>2ᵦ₀</th>
<th>δ</th>
<th>Δₑₚ,m</th>
<th>δ</th>
<th>Δₑ₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg7Fe3R</td>
<td>32.8</td>
<td>0</td>
<td>-0.01</td>
<td>20.8</td>
<td>0.02</td>
<td>0.20</td>
<td>1.36*</td>
<td>1.15*</td>
<td>0</td>
</tr>
<tr>
<td>Mg6Fe4R</td>
<td>33.1</td>
<td>0</td>
<td>0.01</td>
<td>20.6</td>
<td>0.01</td>
<td>0.19</td>
<td>1.46*</td>
<td>1.16*</td>
<td>0</td>
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</table>

Bₘ · m: hyperfine field at maximum of the distribution (T); 2ᵦ₀: quadrupole shifts (mm/s); Δₑₚ,m: quadrupole splitting (mm/s); δ: isomer shifts (mm/s). The values of isomer shifts are with reference to metallic iron. * Fixed parameters.
Table 4. Relative spectral areas (RA values) derived from the Mössbauer spectra of the CNTs-Fe- MgAl$_2$O$_4$ nanocomposite samples measured at room temperature.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mg7Fe3R RA (%)</th>
<th>Mg6Fe4R RA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TMS ILEEMS</td>
<td>TMS ILEEMS</td>
</tr>
<tr>
<td>α-Fe</td>
<td>24 19</td>
<td>24 26</td>
</tr>
<tr>
<td>Fe$_3$C</td>
<td>57 66</td>
<td>49 54</td>
</tr>
<tr>
<td>Fe$^{2+}$ doublet</td>
<td>2 2</td>
<td>1 1</td>
</tr>
<tr>
<td>γ-Fe-C</td>
<td>17 13</td>
<td>26 19</td>
</tr>
</tbody>
</table>

Finally, the study of CNTs-Fe-Al$_2$O$_3$ and CNTs-Fe-MgAl$_2$O$_4$ nanocomposite powders by ILEEMS has given information about the surface state of the powders, demonstrating that ILEEMS is a promising technique complementing transmission Mössbauer spectroscopy for the investigation of the location of the metal Fe and iron-carbide particles in the different CNTs-nanocomposite systems containing iron.

Acknowledgements

This work was partially funded by the Fund for Scientific Research – Flanders, and by the Special Research Fund (BOF, Bijzonder Onderzoeksfonds), UGent (B/06633), Belgium.

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Paper VII

Fe-substituted mullite powders for the in-situ synthesis of carbon nanotubes by catalytic chemical vapor deposition

V.G. de Resende, X. Hui, A. Peigney, A. Weibel, E. De Grave, Ch. Laurent

Fe-substituted mullite powders for the in-situ synthesis of carbon nanotubes by catalytic chemical vapor deposition

Valdirene G. de Resende1,2, Xu Hui2, Christophe Laurent2, Alicia Weibel2, Eddy De Grave1, Alain Peigney2

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Powders of iron-substituted mullite were prepared by combustion and further calcination in air at different temperatures. A detailed study involving notably Mössbauer spectroscopy showed that the Fe$^{3+}$ ions are distributed between the mullite phase and a corundum phase that progressively dissolves into mullite upon the increase in calcination temperature. Carbon nanotube-Fe-mullite nanocomposites were prepared for the first time by a direct method involving a reduction of these powders in H$_2$-CH$_4$ and without any mechanical mixing step. The Fe$^{3+}$ ions present in both the mullite and corundum phases are reduced to form particles that are detected as α-Fe, Fe$_3$C and γ-Fe-C. However, the major part of the Fe$^{3+}$/mullite ions are only partially reduced to Fe$^{2+}$ ions in a hercynite (FeAl$_2$O$_4$) phase. The reducibility of the mullite and corundum phases strongly decreases when the calcination temperature of the catalytic material is higher than 1100°C. The carbon nanotubes formed by the catalytic decomposition of CH$_4$ on the smallest metal particles are mostly double- and multi-walled, although some carbon nanofibers are also observed.

1 Introduction

Ceramic-matrix nanocomposites are one of the many applications of carbon nanotubes (CNTs). One of the main hurdles for the successful preparation of such composites is to obtain a homogeneous distribution of undamaged CNTs into the matrix. To obviate a mechanical-mixing step during the preparation of the composite powder, a direct method for the in situ synthesis of the CNTs into an Al$_2$O$_3$ matrix has been proposed. It is based on a catalytic chemical vapor deposition (CCVD) route involving the reduction in H$_2$-CH$_4$ gas atmosphere of Al$_2$O$_3$-Fe$_2$O$_3$ solid solutions, producing CNTs-Fe-Al$_2$O$_3$ nanocomposite powders. The reduction first produces nanometric Fe particles that are active for the decomposition of CH$_4$, and subsequently for the formation of CNTs, notably single- and double-walled CNTs if their diameter is small enough (< ca. 5 nm). This method was subsequently expanded to powders with MgAl$_2$O$_4$$_5$, MgO$_5$ and ZrO$_2$$_7$ matrix. $^{57}$Fe Mössbauer spectroscopy offers several advantages for studies of iron-containing compounds. The spectra, and
parameters derived from these, are very sensitive to electronic, magnetic and structural characteristics of the probed material and as such, Mössbauer spectroscopy is a useful tool for phase identification and quantification of mixtures of Fe-bearing materials. Although iron species are often involved in CNTs formation processes, only relatively few CNT-related studies, apart from those by some of the present authors,\textsuperscript{4,8-19} report on Mössbauer data with regard to the formation, evolution and the spatial distribution of Fe-containing particles after synthesis of the CNTs by CCVD methods.\textsuperscript{20-24} Mullite is the name of some $\text{Al}_2\text{O}_3$-$\text{SiO}_2$ compounds. The most widely studied form is $\text{Al}_6\text{Si}_2\text{O}_{13}$ (also commonly designated $3\text{Al}_2\text{O}_3:2\text{SiO}_2$) but considerable variations in crystal structure and chemical composition have been found.\textsuperscript{25-30} This material is increasingly important for electronic, optical and high-temperature structural applications, which however are limited by a low toughness. However, CNT-mullite nanocomposites are seldom studied. Wang et al.\textsuperscript{31} prepared such materials by mixing powders of CNTs, $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$. In the present work, the authors for the first time have studied the formation of CNTs from Fe-substituted mullite powders. These catalytic materials and the CNTs-Fe-mullite composite powders will be studied by several techniques including electron microscopy and Mössbauer spectroscopy.

2 Experimental

2.1 Synthesis of the Fe-substituted mullite powders

A combustion method similar to the one reported for the synthesis of pure mullite\textsuperscript{32-34} was used in order to prepare 6 g of $\text{Fe}_{0.6}\text{Al}_{5.4}\text{Si}_3\text{O}_{13}$ powder. The required proportions of $\text{Al(NO}_3\text{)}_3.9\text{H}_2\text{O}$, Fe(NO$_3$)$_3$.9H$_2$O and NH$_4$NO$_3$ (5/6 of the molar quantity of the metal nitrates) were dissolved in an aqueous suspension of colloidal SiO$_2$, using the minimum amount of water. The required proportion of urea (the fuel) was added under continuous stirring up to complete dissolution. The urea proportion was twice the so-called stoichiometric ratio calculated from the total oxidizing valence of the nitrates and the reducing valence of urea.\textsuperscript{35} The dish containing the mixture was placed in a furnace preheated at 600°C, keeping the door of the furnace open. After water evaporation, a combustion reaction takes place between the nitrates and urea, thus producing an oxide powder. The as-prepared powder was divided into several batches, which were calcined in air at different temperatures in the range 800-1400°C (heating rate to the desired temperature equal to 300°C/h, 1 h dwell, natural cooling down to room temperature). The powders are hereafter code-named as C800, ..., C1400.

2.2 Synthesis of the CNTs

The CNT-Fe-mullite nanocomposite powders were prepared by a CCVD treatment in H$_2$-CH$_4$ (20 mol.% CH$_4$, maximum temperature 1050°C, no dwell, heating and cooling rates 300°C/h). The flowing gas was dried on P$_2$O$_5$ and its composition was monitored by mass-flow controllers. The so-obtained powders are named as C800R, ..., C1400R.

2.3 Characterization

X-ray diffraction (XRD) patterns were recorded using a Bruker D4 Endeavor diffractometer equipped with a Cu K$_\alpha$ radiation tube. The carbon content (C$_n$) in the nanocomposite powders was measured by the flash combustion method with an accuracy of $\pm 2\%$. The
specific surface area of the powders was measured by the BET method (Micrometrics Flow Sorb II 2300) using nitrogen adsorption at liquid nitrogen temperature. Mössbauer spectra (MS) at 295 K and 80 K were collected. A spectrometer operating in constant acceleration mode with triangular reference signal and with $^{57}$Co (Rh) source was used. Accumulation of data was made in 1024 channels. The spectrometer have been calibrated by collecting at 295 K the spectrum of a standard hematite ($\alpha$-Fe$_2$O$_3$) or a standard metallic iron foil. The isomer shifts quoted hereafter are referenced with respect to $\alpha$-Fe at room temperature. The powders were observed by field-emission-gun scanning electron microscopy (FEG-SEM, JEOL JSM 6700F). The powders were also observed by high resolution transmission electron microscopy (HRTEM, Jeol JEM 2100F).

3 Results and discussion

3.1 Fe-substituted mullite powders

XRD pattern (Fig. 1) analysis of the as-prepared powder reveals wide peaks characteristic of a poorly crystallized transition alumina. No mullite or iron oxide peaks are detected. According to Burgos-Montes et al., using NH$_4$NO$_3$ as a combustion aid should have allowed for the preparation of crystallized mullite. The difference may be due to the present use of an open furnace, resulting in a less uniform heating, as opposed to a purpose-build reaction device as described by these authors. Peaks characteristic of mullite and peaks accounting for $\alpha$-Al$_2$O$_3$ (corundum) are detected for all calcined powders (Fig. 1). The intensity of the corundum peaks appears to be quite constant for C800-C1100 and regularly decreases for C1200-C1400, possibly revealing its progressive dissolution into the mullite upon the increase in calcination temperature. The mullite peaks become narrower upon the increase in calcination temperature, reflecting crystallite growth. The specific surface area of the C800-C1200 powders is in the range 1.5-4.4 m$^2$/g and is still lower for C1300 (1.0 m$^2$/g) and C1400 (0.5 m$^2$/g). These values are considerably lower than those reported by authors using a very similar method, although the reason for this is not clear.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of the as-prepared powder and after calcination in air at different temperatures m: mullite; and a: corundum. Note that the 20 range shown is not the same for the as-prepared powders and the other ones.

FEG-SEM images of a typical powder (C1100) shows grains several tens of micrometers in size (Fig. 2a). It was not possible to distinguish the mullite from the corundum particles on such images. The grains are made-up of crystallites which are either largely submicrometric,
as shown on a typical higher magnification image for C1200 (Fig. 2b), or micrometric for C1400 (Fig. 2c).

Figure 2. FEG-SEM images of selected powders: C1100 (a), C1200 (b) and C1400 (c).

Mössbauer spectra were recorded at 295 K and 80 K for all calcined powders. In order to check for a possible presence of small amounts of hematite ($\alpha$-Fe$_2$O$_3$) in the samples, three of these were selected and their MS (not shown) collected over a broad velocity scale ($\pm$11 mm/s). The sextet characteristic of hematite was not observed, nor any other sextet component. Consequently, hematite had not been formed in the calcination process, at least not to measurable abundance, in agreement with the XRD results. Thus, in a next stage the MS for all powders were acquired over a narrow velocity scale ($\pm$ 4 mm/s), implying a higher resolution (Fig. 3). All MS are characterized by a broad, slightly asymmetric, doublet shape, which might be explained by the presence of more than one discrete component. This contrasts with earlier studies for Fe-substituted mullite$^{36,37}$ where only a single quadrupole doublet with Mössbauer parameters claimed to be typical for octahedrally coordinated Fe$^{3+}$ was used for the fit. However, the structure of mullite is made up of chains of edge-sharing AlO$_6$ octahedra running parallel to the crystallographic c-axis and cross linked by AlO$_4$ and SiO$_4$ tetrahedra occurring in dimers and trimers.

Figure 3. MS at 295 K of the calcined powders. Fe$^{3+}$/Al$_2$O$_3$ (olive); Fe$^{3+}$/mullite: site A (magenta), site B (yellow) and site C (brown).

The octahedral site bears 66% of the total Al$^{3+}$ ions. The first tetrahedral site contains both Al$^{3+}$ (25% of total) and Si$^{4+}$. The third site is a distorted tetrahedron occupied by 9% of the total Al$^{3+}$ ions. Thus, any of these three sites
may be partly substituted by Fe$^{3+}$. Indeed, several authors proposed a deconvolution of the MS into three doublets: Cardile et al.\textsuperscript{38} and Parmentier et al.\textsuperscript{39} found one octahedral and two tetrahedral sites, whereas Mack et al.\textsuperscript{40} proposed two octahedral and one tetrahedral sites. A three-doublet model indeed produced excellent reproductions of the present MS with no significant mismatches. However, unacceptable inconsistencies in the calculated area fractions of the three components were obvious. A fourth doublet, accounting for Fe$^{3+}$ ions in the α-alumina (corundum) phase, consistent with the identification of this phase in the XRD patterns, was therefore included in the fitting model. No restrictions had to be imposed for the iteration procedure to reach convergency with reasonable parameter values. The adjusted hyperfine parameter values are listed in Table 1. The Fe$^{3+}$/corundum doublet has hyperfine parameters ($\Delta E_Q \approx 0.53$ mm/s and $\delta \approx 0.29$ mm/s at 295 K) that are very close to those found earlier for Fe$^{3+}$ ions in the corundum lattice.\textsuperscript{4,41} The $\Delta E_Q$ values of the three Fe$^{3+}$/mullite doublets are broadly in line with those reported\textsuperscript{38}-\textsuperscript{40} for Fe-substituted mullites. As noted by Parmentier et al.,\textsuperscript{39} differences concerning the distribution of the Fe$^{3+}$ ions among the lattice sites may be attributed to different synthesis routes and thermal treatments. The adjusted values of $\delta$, $\Delta E_Q$ and $\Gamma$ for the four doublets are not significantly affected by the calcination temperature. Interestingly, the area fraction ($RA$) of the Fe$^{3+}$/corundum doublet is more or less constant (≈ 30%) from C800 to C1200, but gradually decreases for C1300 (21%) and C1400 (12%). This finding corroborates the qualitative results of the above XRD analyses showing the progressive dissolution of the Fe-substituted alumina into the Fe-substituted mullite. Although the MS reveal the presence of three distinct Fe$^{3+}$ sites for the mullite phase, the precise nature of the coordination of these respective sites cannot be inferred straightforwardly on the basis of the numerical results. According to the extensive survey of Menil,\textsuperscript{42} room temperature isomer-shift values for Fe$^{3+}$ are found within ranges 0.10 to 0.30 mm/s and 0.28 to 0.50 mm/s for tetrahedral and octahedral sites, respectively. The present $\delta$ values, being equal for all three lattice sites within the estimated error limits of ±0.02 mm/s, are very close to the bordering value between the two types of coordination. Consequently, site assignment exclusively based on the $\delta$ value is not possible in the present case. As mentioned above, one of the tetrahedral site is highly distorted. It is therefore tempting to attribute the doublet with the highest quadrupole splitting (≈1.6-1.7 mm/s - Site C in Table 1) to this site. The relatively large iron-oxygen bond lengths would then explain the relatively high isomer shift values observed for this doublet. Further, it is proposed that none of the two other doublets having smaller quadrupole splittings (Site A and Site B in Table 1) is due to Fe$^{3+}$ in tetrahedral sites, because one would expect to measure a significantly lower isomer shift than the value obtained for the C sites. Therefore, in agreement with Mack et al.,\textsuperscript{40} it is suggested that Site A and Site B both exhibit six-fold coordination. The different values for the respective quadrupole splittings may then be explained by the presence, for one of those sites, of regular tetrahedral as nearest neighbors, while the other one would have tetrahedra with associated oxygen vacancies as nearest neighbors. According to Mack et al.,\textsuperscript{40} this latter octahedral site specifically gives rise to the doublet with the lower quadrupole splitting (Site B in Table 1).
Table 1. Mössbauer hyperfine parameters at 295 K and 80 K of the powders prepared by combustion and further calcination in air.

<table>
<thead>
<tr>
<th></th>
<th>Fe(^{3+}) in alumina</th>
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<th>Fe(^{3+}) in mullite</th>
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<tr>
<td></td>
<td>δ (mm/s)</td>
<td>ΔE(_Q) (mm/s)</td>
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<td>Γ (mm/s)</td>
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<td>C1400</td>
<td>0.41</td>
<td>0.51</td>
<td>12</td>
<td>0.29</td>
</tr>
</tbody>
</table>

\(\Delta E_{Q}\): quadrupole splitting; δ: isomer shifts; Γ: line width; RA: relative spectral areas. The values of isomer shifts are with reference to metallic iron.
3.2 CNT-Fe-mullite composite powders

The XRD patterns of the nanocomposite powders are shown in Figure 4. Mullite and corundum peaks are detected as in the parent oxide powders. Interestingly, α-Fe and hercynite (FeAl$_2$O$_4$) are detected as well.

![XRD patterns of the CNT-Fe-mullite nanocomposite powders](image)

**Figure 4.** XRD patterns of the CNT-Fe-mullite nanocomposite powders; m: mullite; a: corundum; h: hercynite; and Fe: α-Fe. U1 and U2: unidentified peaks.

The intensity of the (110) α-Fe peak is strong for C800R-C1100R, lower for C1200R and C1300R and the peak is not detected for C1400R. It seems that the intensity of the (311) hercynite peak decreases slightly upon the increase of the calcination temperature. Fe$_3$C (cementite) may also be present in some powders but it is difficult to clearly separate the patterns of α-Fe and Fe$_3$C because the respective main diffraction peaks are strongly overlapping. Note that two peaks (labelled U1 and U2 on Figure 4) detected for some powders could not be assigned to any specific phase. Interestingly, it seems that the evolution of the intensity of these peaks more or less follows that for the (110) α-Fe peak.

The carbon content (C$_n$) is constant (2.2 wt.%) from C800R to C1200R, but gradually decreases for C1300R (0.3 wt.%) and C1400R (0.1 wt.%). The specific surface area is higher for C800R, C1000R, C1100R and C1200R (3.9; 6.1; 6.2 and 5.5 m$^2$/g, respectively) than for C1300R (1.4 m$^2$/g) and C1400R (0.7 m$^2$/g). These values tend to be slightly higher than those found for the corresponding catalytic materials. As pointed out earlier, it is the deposition of carbon in the composite powder, particularly in the form of CNTs, which is responsible for most of this supplementary surface area.

Typical FEG-SEM images are shown in Figures 5 and 6. For all powders, long, flexible filaments are observed on the surface of the oxide grains (Fig. 5c, e, f, j). These filaments show a smooth and regular surface, have a diameter smaller than 30 nm and a length of the order of a few tens of micrometers (Fig. 5d, i). From earlier results, it is known that such filaments are isolated CNTs and/or CNTs bundles. The presence of undesirable carbon species, together with CNTs, is also observed in some areas of all the powders. The most frequently observed species are carbon nanofibers (CNFs - Fig. 5b, d, h), easily detectable by their rough surface and their diameter in the range 30-80 nm. Some carbon nanoribbons (CNRs), 50-100 nm in width (Fig. 5b, j, 6b) are rarely observed. Fe or Fe$_3$C spherical nanoparticles (NPs), with a diameter in the range 5-20 nm, are also observed on the surface of some oxide grains particularly when the grains are not completely covered by a thick layer of carbon filaments (Fig. 5c, 6e). Significantly less CNTs are observed for
powders C1300R (Fig. 6c-e) and C1400R (Fig. 6f, g), in agreement with their much lower carbon content (0.3 and 0.1 wt. % respectively) compared to the other powders (2.2 wt. %). For the powders C800R, C1000R and C1100R, some grains are homogeneously covered by a network of CNTs, without any CNFs or CNRs (Fig. 5c, e, f, i, j) but other areas or grains are covered by a mixture of CNTs, CNFs and a few CNRs (Fig. 5a, b, d, g, h). A similar mixture is observed for C1200R (Fig. 6a, b). For C1300R, rare grains covered by CNTs and numerous NPs are observed (Fig. 6e).

Disordered carbon is observed at the surface of some CNTs, but a fair proportion of it was formed during the observation because the CNTs, notably the thinner ones, were damaged by the electron beam.

Figure 5. FEG-SEM images of the CNT-Fe-mullite nanocomposite powders: C800R (a-c), C1000R (d-f), C1100R (g-j).

Typical HRTEM images show the different carbon species, including a carbon nanofiber (Fig. 7a), a CNTs bundle (Fig. 7b), a Fe or Fe₃C particle covered by graphene layers (Fig. 7c), double-walled CNTs (Fig. 7d-f) and multi-walled CNTs (Fig. 7g-j).

Figure 6. FEG-SEM images of the CNT-Fe-mullite nanocomposite powders: C1200R (a, b), C1300R (c-e) and C1400R (f, g).

Figure 7. Typical HRTEM images showing a carbon nanofiber (a), a CNTs bundle (b), a Fe or Fe₃C particle covered by graphene layers (c), double-walled CNTs (d-f) and multi-walled CNTs (g-j).
The MS at 80 K of the reduced powders are shown in Figure 8 and the corresponding Mössbauer parameters are summarized in Table 2. All spectra have been analyzed using Lorentzian line shapes. In general eight components were found to be required to obtain adequate fits: (i) an outer sextet showing hyperfine parameters that are characteristic of $\alpha$-Fe, (ii) an inner sextet that was fitted with parameters of Fe$_3$C, (iii) a singlet that corresponds to a $\gamma$-Fe phase, possibly alloyed with carbon ($\gamma$-Fe-C), (iv) an Fe$_{3+}$ doublet due to iron ions in the lattice of corundum, and (v-viii) four Fe$^{2+}$ doublets that were assigned to ferrous iron in tetrahedral and octahedral sites of hercynite. Additionally, a ninth Fe$_{3+}$ doublet was needed to be included in the fit of the spectrum of sample C1400R. Its quadrupole splitting was found to be approximately 1.03 mm/s and isomer shift $\sim$0.49 mm/s. This Fe$_{3+}$ doublet could also be due to hercynite. Indeed, Larsson et al. obtained a spectrum, of a very disordered sample, that was fitted using four Fe$^{2+}$ doublets and one Fe$^{3+}$ doublet which had hyperfine parameters ($\Delta E_Q$ $\sim$0.95 mm/s and $\delta$ $\sim$0.47 mm/s) very similar to the ones found in this work. Interestingly, no contribution for Fe$_3$/mullite was detected. The RA values corresponding to the Fe$_3$/corundum were found in the range 8-16 %. The total contribution for hercynite is similar (33-36%) for C800R, C1000R and C1100R. An increase is observed for C1200R (44%), C1300R (62%) and C1400R (92%). The $\alpha$-Fe contribution in the MS is similar (41-42%) for C800R, C1000R and C1100R. A decrease of this contribution is observed for C1200R (28%) and C1300R (24%). For C1400R, there is no $\alpha$-Fe contribution. A similar evolution is observed for $\gamma$-Fe-C. Fe$_3$C was detected in only three of the nanocomposites (C1000R, C1100R and C1200R). The Fe$_3$C contribution is weak (< 7%) and therefore, the corresponding hyperfine parameters had to be kept fixed in the fit procedures and letting free only the hyperfine field.

Figure 8. MS at 80 K of the CNT-Fe-mullite nanocomposite powders. Fe$_{3+}$/Al$_2$O$_3$ (olive); $\alpha$-Fe (red); Fe$_3$C (blue); $\gamma$-Fe-C (cyan); Fe$^{2+}$/hercynite (dark yellow, violet, green, light gray) and Fe$^{3+}$/hercynite (navy).

For the sake of clarity, the evolution of the proportions of the iron species in hercynite, corundum and the reduced phases ($\alpha$-Fe, $\gamma$-Fe-C and Fe$_3$C) versus the calcination temperature of the oxide catalytic material is presented in Figure 9a. It clearly appears that the content of the reduced forms of iron ($\alpha$-Fe, $\gamma$-Fe and Fe$_3$C) sharply diminishes when the calcination temperature is higher than 1100°C which is correlated with the increase of the proportion of the iron species in hercynite. Earlier studies have revealed that either no detectable amounts or only a small amount (≤ 11 %) of hercynite is formed upon the H$_2$-CH$_4$ reduction when the catalytic material is an Al$_2$O$_3$-Fe$_2$O$_3$ solid solution (i.e. a Fe$_{3+}$/corundum phase). Therefore, the Fe$^{2+}$ ions in hercynite
detected in the present powders are mostly produced by the reduction of the Fe$^{3+}$ ions that were present in mullite in the catalytic material. The total proportion of the reduced species is higher than the proportion of the Fe$^{3+}$/corundum in the starting material, which shows that a fraction of the reduced species is formed by the reduction of the Fe$^{3+}$/mullite, with or without the formation of intermediate Fe$^{2+}$/hercynite. However, the calculation of a reduction ratio from the respective proportions of, on the one hand, Fe$^{3+}$/corundum in the starting material (Table 1) and in the nanocomposite powders (Table 2), and, on the other hand, of Fe$^{3+}$/mullite (Table 1) and Fe$^{2+}$/hercynite (Table 2), reveals that the reducibility of both phases is much hampered when the calcination temperature is higher than 1100°C (Fig. 9b).

4 Conclusions

Powders of iron-substituted mullite have been prepared by combustion and further calcination in air at different temperatures. A detailed study involving notably Mössbauer spectroscopy evidenced that the iron ions are distributed between the mullite phase and a corundum phase that progressively dissolves into mullite upon the increase in calcination temperature. Using these powders as catalytic materials has for the first time permitted to prepare CNT-Fe-mullite nanocomposites by a direct method involving a reduction in H$_2$-CH$_4$ and without any mechanical mixing step. The Fe$^{3+}$ ions present in both the mullite and corundum phases are reduced to form metallic particles that are detected as α-Fe, Fe$_3$C and γ-Fe-C. However, the major part of the Fe$^{3+}$/mullite ions are only partially reduced to Fe$^{2+}$ ions in a hercynite (FeAl$_2$O$_4$) phase. The reducibility of the mullite and corundum phases is much hampered when the calcination temperature of the catalytic material is higher than 1100°C. The CNTs formed by the catalytic decomposition of CH$_4$ on the smallest metal particles are mostly double- and multi-walled, although some carbon nanofibers are also observed.

Figure 9. a) The evolution of the proportions of the iron species in the reduced phases (α-Fe, γ-Fe-C and Fe$_3$C) (open square), corundum (solid square) and hercynite (triangle) versus the calcination temperature of the catalytic material. b) Reduction ratio for the corundum (solid square) and mullite phases (open square); see text for details.

Acknowledgements

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Table 2. Mössbauer hyperfine parameters at 80 K of CNT-Fe-mullite nanocomposite powders.

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Fe\(^{3+}\) in hereynite

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<td></td>
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\(^1\)Fixed parameters
\(^2\)In that sample an extra Fe\(^{3+}\) doublet is present: \(\delta \sim 0.49\) mm/s; \(\Delta E_Q \sim 1.03\) mm/s; \(\Gamma \sim 0.52\) mm/s; RA \sim 13%.

\(B_{hf}\): hyperfine field; \(\Delta E_Q\): quadrupole splitting; \(\delta\): isomer shifts; \(\Gamma\): line width; RA: relative spectral areas. The values of isomer shifts are with reference to metallic iron.
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**A3 journals**
