Inhibiting the Carbon Deposition from the Reverse Boudouard Reaction in Refractories Submitted to CO–H₂ Atmosphere

J. Poirier, J. Kadok, N. Bost, A. Coulon, M. R. Ammar, S. Brassamin, C. Genevois

The catalytic decomposition of carbon monoxide via the reverse Boudouard reaction in the presence of a mixture of CO–H₂ gas produces a solid sp² carbon deposit, which has deleterious effects on refractory materials. The catalytic effects of iron oxides and the structural evolution of carbon during the reverse Boudouard reaction in CO–H₂ atmosphere is investigated at a nano and micro-scale. Sulphur compounds inhibit the carbon monoxide dissociation on contact with iron and iron oxides. The samples were characterised by X-ray diffraction, Raman spectroscopy, scanning and transmission electron microscopy. A mechanism that governs the inhibition of the reaction is proposed and validated at lab scale, in which the formation of a very thin protective FeS layer (0.5–1 nm) is involved. This research is applied to develop new CO/H₂ resistant refractories.

1 Introduction

The mechanism of carbon monoxide decomposition, called the reversed Boudouard reaction:

\[ 2\text{CO} \rightarrow \text{CO}_2 + \text{C} \]

results in the deposition of sp² solid carbon. This C deposition, inside the porosity of the refractory, causes premature degradation of linings, which operate under reducing atmosphere [1]. The destruction of refractory materials in CO atmosphere is well explained in the literature [2].

The refractory damage process includes four steps:

- Diffusion of CO gas diffusion into the porosity of the refractory material;
- Reduction of iron oxides into iron then carburization into Fe₃C, which then acts as a catalyst for C-decomposition according Fe₃C → 3 Fe + C;
- Nucleation and growth of the carbon deposition, which generate thermomechanical stress inside the refractory;
- Formation of cracks, damage then destruction of the refractory.

This reaction occurs at temperature ranging between 400–900 °C with a maximum intensity around 600 °C and is highly favoured by the presence of catalytic particles such as iron and iron oxides. Fe₂O₃ and Fe particles are present in the refractories as secondary mineral phases in raw materials and as impurities due to crushing and mixing while blending the refractory formulation. The CO resistance is usually improved by the selection of raw materials with a low content of iron particles and by increasing the refractory sintering temperature (Fe ions are adsorbed in the lattice or bonded in the glassy phase). However, these solutions are not always very effective for industrial applications (such as low-CO blast furnace process, biomass gasification reactors, steam methane reformers, direct reduction shafts, reactors in the petrochemical industry, etc.) where refractories are subjected to CO and H₂ extremely reducing atmospheres.

According to the literature, two reactions explain the carbon deposition phenomena in a temperature range between 400–1050 °C:

- The reverse Boudouard reaction
  \[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \]
  \[ \Delta H^\circ = -172.4 \text{ kJ/mol} \]
  \[ K_1 = \frac{P_{\text{CO}_2} \cdot a_C}{P_{\text{CO}} (1)} \]
  (1)

- The reverse water gas reaction
  \[ \text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O} \]
  \[ \Delta H^\circ = -131.3 \text{ kJ/mol} \]
  \[ K_2 = \frac{P_{\text{H}_2} \cdot a_C}{P_{\text{CO}} \cdot P_{\text{H}_2O}} \]
  (2)

From reactions (1) and (2), the water-gas shift reaction (WGSR) describes the reaction of carbon monoxide and water vapour to form carbon dioxide and hydrogen

\[ \text{CO} + \text{H}_2 \text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

\[ \Delta H^\circ = -41.166 \text{ kJ/mol} \]

\[ K_3 = \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2}}{P_{\text{CO}} \cdot P_{\text{H}_2O}} \]

(3)

In direct reduction processes, the decomposition of methane into carbon also occurs

\[ \text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2 \]

\[ \Delta H^\circ = 92.676 \text{ kJ/mol} \]

\[ K_4 = \frac{P_{\text{H}_2} \cdot a_C}{P_{\text{CH}_4}} \]

(4)

Keywords: Boudouard reaction, carbon deposition, refractory damage, cementite, sulphur

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In reactions (1–4), $K_1$, $K_2$, $K_3$, $K_4$ are the equilibrium constants of reactions, $P_{\text{CO}}$, $P_{\text{CO}^2}$, $P_{\text{H}_2}$, $P_{\text{H}_2O}$, $P_{\text{CH}_4}$ the partial pressures of CO, CO$_2$, H$_2$, H$_2$O, CH$_4$ and $a$, the carbon activity. The effect of H$_2$ in CO increases significantly the reaction of carbon deposition. For example, Walker, et al. [3], report a deposition of 10 g of solid carbon after ~350 min over 0,10 g of carbonyl iron in 9 %-H$_2$–91 % CO gas mixture during 5 h at 600 °C.

Fig. 1 illustrates this reaction. Few grams of Fe$_2$O$_3$ were submitted to 71 % CO, 3 % CO$_2$, 11 % H$_2$, 15 % N$_2$ gas mixture during 5 h at 600 °C under atmospheric pressure. A large amount of carbon formation was observed similar to a “popcorn” formation. The hydrogen content in the CO has an effect of Fe$_2$O$_3$ particles mixed with solid sulphur and with SO$_2$ was mixed continuously with the reducing CO/H$_2$ gas. Measurements of Fe$_2$O$_3$ mass variation were performed using a thermobalance from NETZSCH STA 409C/CD coupled with a QMS 403/5 Skimmer. Fe$_3$O$_4$ samples of approximately 30 mg were placed in an alumina crucible and were heated to 600 °C at a rate of 10 °C · min$^{-1}$ under 100 ml · min$^{-1}$ of an argon inert gas prior to being exposed to a reducing CO/H$_2$ gas (100 ml · min$^{-1}$).

The crystalline phases were analysed with powder X-ray diffraction using a Bruker D8 A25 diffractometer (Bragg-Brentano geometry θ-θ) equipped with a LynxEye XE detector and using the Cu $K_\alpha$ radiation ($\lambda = 1,5418$ Å). Raman spectroscopy was performed using a T64000 Jobin-Yvon multichannel spectrometer equipped with an Ar–Kr laser source, an X41 Olympus microscope and a liquid nitrogen-cooled CCD detector. The spectra were collected in a backscattering geometry under a microscope (~20 long working distance objective) using the 514,5 nm wavelength (2,41 eV; 3 mW of laser power), a 600 groves · mm$^{-1}$ grating giving a spectral resolution of 3 cm$^{-1}$ in the 1000–2000 cm$^{-1}$ wavenumber range. Heating the sample was achieved using a TS1500 Linkam device (Tadworth/GB).

The same temperature program was used for Raman spectroscopy and for TGA (10 °C · min$^{-1}$ until 600 °C). After the experiments, the samples were also characterised by scanning electron microscopy (Hitachi S4500 FEG) and high resolution transmission electron microscopy (Philips CM20 microscope).

Scanning transmission electron microscopy (STEM-HAADF) images were acquired in the angular range of 50–180 mrad with an 8 cm camera length and a 0,1 nm probe size. Elemental composition line scans were performed by STEM-EDS using a JEOL EDS system and a 0,13 nm probe size.
3 Effect of iron oxides on the carbon formation in CO, H₂ atmosphere [2]

3.1 Effect of Fe₂O₃ grain size on the rate of carbon formation

Fe₂O₃ with different grain sizes (35 nm, <5 µm, 160–250 µm and 1–2 mm/purity >99 %) was used. Initial specific surfaces of the particles are below 10 m²/g, excepted for the 35 nm size (42 m²/g). Fig. 2 a shows the variation in the sample weight (full lines) based on the thermogravimetric measurements (TGA) as well as the variation in the temperature (black dashed line) as a function of time. At 600 °C, the samples were subjected to a CO/H₂ gas mixture (composition R: 71 % CO, 3 % CO₂, 11 % H₂, 15 % N₂) for 5 h.

As soon as the gas was injected (at approximately 130 min), a weight loss (approximately 25 mass-% for the nanometre grain size) that was associated with the reduction of the Fe₂O₃ phase in competition with the production of solid carbon was observed. After this reduction, a rapid increase in the weight of the samples was observed (Fig. 2 a). This weight gain was primarily due to the production of solid carbon and corresponded to a catalyst/carbon deposition ratio of approximately 1/100 within the asymptotic limit of the Fe₂O₃ sample. Fig. 2 b shows the normalised weight curve using an asymptotic function of the curves shown in Fig. 2 a. According to the data, the production of carbon appears to be independent of the grain size of the catalyst; the size of the initial grain is not an important parameter for controlling the rate of carbon deposition. However, the smallest grains (35 nm) were slightly more reactive and formed more carbon than the largest grains. The largest grains exhibited the slowest formation and produced less carbon.

3.2 Effect of the iron valence on the carbon deposition rate

Pure iron and iron oxides (FeO, Fe₂O₃ and Fe₃O₄) powders were submitted for 5 h at 600 °C under reducing atmosphere (composition R 70 % CO, 10 % H₂, 3 % CO₂ and 17 % N₂). The gas flow was 4,2 l/h. Results are reported in Fig. 3 a. As soon as the gas was injected (at 130 min), a weight loss (≈ 25 % for Fe₂O₃; Fig. 3 b) that was associated with the chemical reduction of the Fe₂O₃ phase occurs. After this reduction, a rapid increase in the weight of all of the samples was observed, except for the FeO sample, which requires a longer reaction time (≈ 50 min). The reaction produces a large amount of solid carbon (Fig. 3 c).

The Fe₂O₃ particles are reduced to metallic iron by the hydrogen. This phenomenon has been described in the literature [3, 4]. In a mixture consisting of CO+H₂ gas, there are many competing reactions including chemical reduction of iron oxides, carbon deposit via the reverse Boudouard reaction, and water and carbon formation via the reverse water-gas reactions. It is impossible to distinguish these different reactions in thermogravimetric measurements.

![Fig. 2 a–b a) Mass variation of Fe₂O₃ samples versus time depending to the temperature (in black dotted line); b) mass normalised curve](image1)

![Fig. 3 a–c a) Mass variation of the sample as a function of time and temperature (in dotted line); b) enlargement of the Fig. 3 a; c) carbon deposition in the crucible for the Fe₂O₃ samples](image2)
Complementary measurements: XRD and SEM observations (Fig. 4) show the quasi complete transformation of a few milligrams of FeO in pure cementite phase (Fe₃C). The sp² type carbon is formed and is favoured by the catalyst particles. The catalyst grains are highly fragmented to nanometre-sized grains independently of the initial grain size, due to hydrogen effect and the chemical reduction. During the experiment, the FeO particles were substantially reduced in size.

### 4 Effect of sulphur compounds on the inhibition of the carbon formation

This part presents an efficient method to inhibit the carbon deposit from the reverse Boudouard reaction catalysed by the FeO oxides: a low quantity of sulphur additions prevents the formation of carbon [5]. TGA experiments were performed to quantify the effect of inhibiting sulphur on carbon growth rate as a function of the S amount in the various solid or gaseous mixtures.

#### 4.1 Effect of solid sulphur on the amount of carbon produced by the Boudouard reaction

TGA experiments were performed to validate the effect of inhibiting sulphur compounds on carbon formation, and to quantify the carbon growth rate in function of the S amount and sulphur species in the various mixtures. FeO powders were mixed with sulphur with different amount (1, 5, 10 and 30 mass-% S respectively) and with sulphates (1 mass-% BaSO₄, 1 mass-% CaSO₄, 1 mass-% MgSO₄). Fig. 5 a–b shows TGA results (mass variation as a function in time) and are compared to an experiment without sulphur or sulphates additions.

During heating, in inert atmosphere (100 ml · min⁻¹ Ar), FeO + S mixtures have a mass loss associated with sulphur vaporization at 443 °C, proportional to the amount of the introduced S (Fig. 5 a). This loss of mass is not observed for the mixtures: FeO – 1 mass-% BaSO₄, CaSO₄, MgSO₄ (Fig. 5 b). Indeed, the decomposition of sulphates and thus the volatilization of S occur at temperatures above 600 °C. As soon as the CO/H₂ reducing gas is injected, a weight loss (approximately 25 mass-%) is observed which is due to the chemical reduction of the iron oxides by hydrogen. The FeO sample (reference) shows a very important carbon deposit. The samples containing sulphur and sulphates have a very low weight gain that stabilizes after 200 min.

#### 4.2 Effect of S gas on the amount of carbon produced by the Boudouard reaction

The continuous injection of gaseous sulphur has many advantages compared to a solid sulphur addition. It allows providing a sustainable amount of sulphur and thus, a more efficient inhibition of carbon formation. The experiments were carried out with

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**Fig. 4 a–b** XRD diffractograms of the FeO samples and backscattered images initial sample FeO <5 µm; b) after the CO–H₂ reaction, the size of particles is reduced.

**Fig. 5 a–b** TGA curves of the samples exposed to the reducing gas mixture at 600 °C:

- a) mixture of FeO powders and pure S (1, 5, 10 and 30 mass-%, respectively);
- b) mixture of FeO powders and sulphates (1 mass-% BaSO₄, 1 mass-% CaSO₄ and 1 mass-% MgSO₄)
Fe$_2$O$_3$ at 600 °C under a CO/H$_2$ reducing gas containing SO$_2$.

Fig. 6 shows TGA results (mass variation as a function of time) for SO$_2$ contents equal to 1, 10, 50, 100 and 1000 ppm, respectively and compared to an experiment without SO$_2$ addition. Once the gas mixture is injected, all samples underwent a similar mass loss for about 20 min. This is the consequence of the Fe$_2$O$_3$ reduction into pure iron prior to its carburation in iron carbide [6]. For the samples exposed to a gas mixture containing 1–10 ppm of SO$_2$, a dramatic mass gain is observed due to carbon formation; roughly like what could be found without SO$_2$. When 50 ppm of SO$_2$ was injected, a lower mass gain is observed, and the carbon growth rate has been decreased by a factor 7.5 in comparison with the experiment without SO$_2$. For 100 ppm and 1000 ppm of SO$_2$, the carbon growth rate values have been decreased by a factor 70. However, a slightly higher mass gain is observed for the sample with 100 ppm of SO$_2$ in comparison with 1000 ppm.

4.3 Structural evolution of the carbon

4.3.1 Raman spectroscopy

Raman spectroscopy is an ideal technique to characterize in situ sp$^2$ carbon materials. It is the most sensitive to explore the full range of the structural states from perfectly crystalline to amorphous [7].

The typical Raman spectrum of sp$^2$ carbon is reported in Fig. 7 c and shows three prominent features. The so-called G band located at approximately 1580 cm$^{-1}$ corresponds to the in-plane bond stretching of carbon atoms (E$_{2g}$ symmetry). When defects are present, the crystal symmetry breaks down and additional bands appear at specific frequencies depending on the excitation energy used. These bands are called the defect bands: D ($\approx 1250–1400$ cm$^{-1}$) and D' ($\approx 1600–1630$ cm$^{-1}$). At relatively low defect density, the intensity ratio of the defect-induced D band and the symmetry-allowed G band increases with disorder.

Pure iron and iron oxides powders were submitted for 30 min at 600 °C under reducing atmosphere: 100 % CO and CO/H$_2$ mixture. Fig. 7 summarizes the results obtained using Raman spectroscopy and TEM. Raman spectra of the carbon formed in the two types of gas are totally different. G band is observed in the carbon formed under 100 % CO, and D and G bands are observed when the gas is a mixture of CO and H$_2$.

In CO atmosphere, well organised sp$^2$ carbon is formed around the catalyst particles and the defect-induced D bands are not observed. Only chemical reduction of the catalyst particle occurs without significant size reduction. Therefore, poly-aromatic layers are formed around the catalyst particles in the form of encapsulating shells. These layers are sufficiently large with regards to the laser diameter which explains the no activation of the defect-induced D band in the corresponding Raman spectrum [6]. In CO + H$_2$ atmosphere, the corresponding Raman spectrum exhibits the defect induced D band suggesting disordered carbon. Catalyst particles are chemically reduced and
4.2.2 Microscopic characterisation of samples

To better understand the effect of sulphur on the inhibition of the carbon produced by the reverse Boudouard reaction catalysed by Fe$_2$O$_3$, the samples were observed after TGA experiments, by Scanning Electron Microscopy (SEM) and High-Resolution Transmission Electron Microscopy (HRTEM).

Highly fragmented. Therefore, small-sized carbon nanofibres are formed exhibiting a large amount of poly-aromatic boundaries. This eventually leads to the activation of the defect induced D band without the local structural order being necessarily disturbed [6].

Fig. 8 reported the FWHM$_G$ versus $I_D/I_G$ for all the samples at each gas. According to [8], this graphic show the evolution of the "crystallite size and defect" of the carbon. The most well crystalline sp$^2$ carbon is natural graphite, and it plotted closed to the origin of this graph (orange circle). The less organised carbon could be ideally in the top of this diagram (Fig. 8) with FWHM$_G$ upper to $\approx 70$ cm$^{-1}$. Fig. 8 a shows the results for the carbon obtain to a 100 % CO gas. All the data are very close to the bottom part of the diagram with a moderate FWHM$_G$, due to the temperature of the experiment. As mentioned above, this result is in accordance with the lack of D band on the Raman spectra, due to the morphology of carbon in onion. The addition of 5 % of hydrogen in the gas mixture induce a moved to the right part of the diagram (Fig. 8 b), with an important increase of the FWHM$_G$. The increase of the H$_2$ content favoured an increase of the $I_D/I_G$ ration and a relative staggering of the point (Fig. 8 c). This spreading should be moderated by the low quality of Raman spectra obtained for this test. The experiment using an analog of industrial gas (Fig. 8 d) with a CO/H$_2$ ratio closed to the gas mixture C, shows results similar to the data obtains in Fig. 8 c.

Fig. 8 Evolution of G band width at half-maximum (FWHM$_G$) versus the intensity ration of the D relative to G band of series of in situ measurement of carbon formed under different iron catalyst at different gases at 600 °C (except for C at 500 °C)
The rounded shape of these particles may suggest a molten state. This observation was previously observed between 800–1000 °C [9,10], and explained by Krause and Pötschke [1]: In the binary phase diagram Fe–C, the eutectic melting point drop from 1153 °C to temperature lower than 500 °C, and at this temperature droplets of carbon bearing iron are visible.

The sample exposed to 1000 ppm of SO\textsubscript{2}(g) exhibits a quite different morphology. EDS analysis reveals only the presence of iron carbide particles such as Fe\textsubscript{3}C and/or Fe\textsubscript{5}C\textsubscript{2} according to XRD. Considering their sizes, those particles do not seem to have been fragmented or fragmented to a lesser extent. A TEM micrograph for a sample exposed to 1000 ppm of SO\textsubscript{2}(g) is presented in Fig. 10 a. No filamentous carbon is observed on the micrograph and the iron carbide particles are systematically covered by a nanometer-sized thick shell. High resolution STEM-HAADF images show a two-layered shell (Fig. 10 b–c) The inner layer is very thin (0.5–1 nm). This inner layer is rich in sulphur with a rather high content of iron, which suggests the formation of an FeS iron sulphide.

5 Discussion about the mechanisms of carbon formation and carbon inhibition by sulphur

Under 100 % CO atmosphere, the carbon formation by the Boudouard reaction is a well known process. The iron oxides are reduced by CO and converted to iron carbide (cementite). Liquid iron/Fe\textsubscript{3}C nanometric droplets are formed which dissolve carbon until the saturation limit. Carbon is segregated on the liquid surface droplet [1]. The catalytic deposit of carbon originates from a dissolution-precipitation mechanism of carbon.

The carbon has a high structural organisation and forms polyaromatic shells around big catalytic oxide particles. When hydrogen is present, the reactions become more efficient. The phase transformations (Fe\textsubscript{x}O\textsubscript{y} → FeO → Fe → Fe\textsubscript{3}C) result in a dramatic increase in the specific surface areas of catalytic particles. H\textsubscript{2} favours the nucleation and growth of carbon fibres on the iron-carbide particles.

Fig. 11 reports the different steps of the formation of carbon nanofibers by the reverse Boudouard reaction in CO–H\textsubscript{2} atmosphere:

**Fig. 9** a–d TEM micrograph of nano-carbon filaments for different catalysts formed at 600 °C in: a) 71 % CO, 3 % CO\textsubscript{2}, 11 % H\textsubscript{2} and 15 % N\textsubscript{2} a Fe\textsubscript{2}O\textsubscript{3} 35 nm; b) Fe\textsubscript{2}O\textsubscript{3} 1–2 mm; c) Fe\textsubscript{3}O\textsubscript{4} <5 µm; and d) FeO 2–5 µm

**Fig. 10** a–c Micrographs of the sample after TGA experiments exposed to 1000 ppm of SO\textsubscript{2}(g): a) TEM image representative of the sample; b), c) high resolution HAADF-STEM images of a particle surrounded by a two-layer shell
• Step 1: reduction by \( \text{H}_2 \) and \( \text{CO} \) with formation of suboxides of iron (\( \text{Fe}_2\text{O}_3 \rightarrow \text{FeO} \rightarrow \text{Fe} \)) recrystallization of particles and decrease of iron oxide size to nanometer-sized particles;
• Step 2: liquid iron/ \( \text{Fe}_3\text{C} \) nanometric droplets;
• Step 3: grow of polyaromatic carbon nanofibres.

The mechanism of the carbon formation is inhibited by sulphur or sulphates additions. This result is confirmed by 20 h experiments in laboratory. On the surface of the iron oxide particles, \( \text{FeS} \) or \( \text{FeS}_2 \) iron sulphides are formed (Fig. 12). The formation of these sulphides can be partial or total depending on the size of the iron oxide particles, the heating time and the reaction time.

Sulphur does not prevent the reduction of \( \text{Fe}_2\text{O}_3 \) by \( \text{H}_2 \) and \( \text{CO} \) and the fragmentation of the \( \text{Fe}_2\text{O}_3 \) grains. Nevertheless, it limits the formation of sp\(^2\) carbon. Sulphur diffuses into the crystallite structure or through the grain boundaries. Moreover, it is not necessary to transform all the iron into iron sulphides to inhibit the carbon deposition by the reverse Boudouard reaction.

However, the \( \text{FeS} \) layer is not stable, \( \text{S} \) adsorption is a dynamic phenomenon and there are always some defects in the \( \text{FeS} \) layer which will lead to a slow continued carbon formation.

Fig. 13 reports the mechanism of carbon inhibition in \( \text{CO}–\text{H}_2 \) atmosphere.

6 Implication for industrial processes

The carbon formation from the Boudouard reaction and the nanocarbon formation were extensively studied for the last two decades. Nowadays, this phenomenon appears to be highly important for the development of new high temperature industrial processes. For example, in new energy field, the biomass and the waste gasification or the low C blast furnaces are highly vulnerable when the Boudouard reaction occurs. The refractory lining of these reactors could be highly damaged. Moreover, \( \text{CO}–\text{H}_2 \) gas will be efficiently used for reducing the power cost of industrial processes, and a technical solution should be developed for preserved refractory materials. Indeed, all these new developments are in relation with the global objective of reducing greenhouse gas emissions. The injection of \( \text{H}_2 \) gas...
in CO mixture in refractory devices developed new challenges with the limitation of the damage of ceramics material. This destruction was well controlled in the case of only CO by empirical knowledge of reconstruction was well controlled in the case of the damage of ceramics material. This developed new challenges with the limitation of CO mixture in refractory devices in the future industrial atmosphere. Consequently, this study is helpful for the development of laboratory and industrial solutions, for example by modification of carbon morphology.

The benefit effect of S to inhibit the formation of carbon was applied to develop CO/H₂ resistant refractories. Laboratory experiments were made using a commercial castable. The chemical composition [mass-%] of the castable is:

<table>
<thead>
<tr>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>81</td>
<td>16</td>
<td>2,5</td>
<td>0,6</td>
</tr>
</tbody>
</table>

To promote the formation of carbon and to increase the degradation of refractories, 5 mass-% Fe₂O₃ nanoparticles were mixed. Three different formulae were prepared, and a low quantity of sulphur was incorporated in two samples:
- C1: castable + 5 mass-% Fe₂O₃;
- C2: castable + 5 mass-% Fe₂O₃ and 0.5 mass-% solid sulphur;
- C3: castable + 5 mass-% Fe₂O₃ and 3.3 mass-% BaSO₄.

After curing, the three castables were pre-fired in air at 900 °C, for 8 h. Then, they were submitted, for 5 h, at 600 °C under CO + H₂ reducing atmosphere (composition R). Reference powders of pure iron oxide were also tested under the same experimental conditions. The castable C1 (with 5 mass-% Fe₂O₃) was destroyed by a “bursting reaction”. A significant carbon deposit in the cementitious matrix was observed and analysed by Raman spectroscopy. The castables C2 and C3 containing S and BaSO₄ additives did not exhibit significant carbon deposit and were not damaged by the reverse Boudouard reaction (Fig. 14). These results were confirmed by Thermogravimetric Analyses (TGA), under reducing atmosphere: composition R: 71 % CO, 3 % CO₂, 11 % H₂, 15 % N₂.

However, the effect of S additives to inhibit the formation of carbon has limits: the sulphur additives become ineffective beyond 900 °C. In some industrial applications, the refractories are subjected to cyclic conditions: oxidising and reducing. Under these conditions, the stability of FeS and FeS₂ is not guaranteed. An addition of sulphurous gas (100 ppm) in CO/H₂ gas should be an effective solution to limit the carbon formation and the damage of refractories.

7 Conclusion

The carbon deposit in refractories is catalysed by iron and iron oxides. This reaction is highly favoured by the presence of H₂. The mechanism of the catalytic decomposition of carbon monoxide via the Boudouard in the presence of H₂ is better understood. Two different carbons are formed in specific gas composition. In 100 % CO, the sp² carbon has a high structural organisation with important coherent domain diameter and formed polyaromatic shells around relatively big catalytic particles.

The addition of H₂ in CO favours the formation of polyaromatic carbon with nanofibre morphology. This morphology of carbon could be the cause of the destruction of refractory materials test in CO + H₂ atmosphere. Laboratory experimentations showed that sulphur additives inhibited the CO dissociation and the formation of carbon. The practical conclusions of this study will be applied to develop new CO/H₂ resistant refractories.

References


![Fig. 14 Carbon deposit and destruction of C1 (a); effect of sulphur on C2 and C3 castables after exposure to reducing gas (b)](image-url)