# Thermal and mechanical behaviour of oxygen carrier materials for chemical looping combustion in a packed bed reactor



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# Thermal and mechanical behaviour of oxygen carrier materials for chemical looping combustion in a packed bed reactor

M. Jacobs [a,*], J. Van Noyen [b,1], Y. Larring [c], M. Mccann [c], M. Pishahang [c], S. Amini [c], M. Ortiz [d], F. Galluci [d], M.V. Sint-Annaland [d], D. Tournigant [e], E. Louradour [e], F. Snijkers [a]

[a] VITO, Belgium
[b] Dow Chemicals, The Netherlands
[c] SINTEF, Norway
[d] TU/e, The Netherlands
[e] CTI, France

## HIGHLIGHTS

- Ilmenite-based oxygen carriers were developed for packed-bed chemical looping.
- Addition of $Mn_2O_3$ increased mechanical strength and microstructure of the carriers.
- Oxygen carriers were able to withstand creep and thermal cycling up to 1200 °C.
- Ilmenite-based granules are a promising shape for packed-bed reactor conditions.

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## ABSTRACT

Chemical looping combustion (CLC) is a promising carbon capture technology where cyclic reduction and oxidation of a metallic oxide, which acts as a solid oxygen carrier, takes place. With this system, direct contact between air and fuel can be avoided, and so, a concentrated $CO_2$ stream is generated after condensation of the water in the exit gas stream. An interesting reactor system for CLC is a packed bed reactor as it can have a higher efficiency compared to a fluidized bed concept, but it requires other types of oxygen carrier particles. The particles must be larger to avoid a large pressure drop in the reactor and they must be mechanically strong to withstand the severe reactor conditions. Therefore, oxygen carriers in the shape of granules and based on the mineral ilmenite were subjected to thermal cycling and creep tests. The mechanical strength of the granules before and after testing was investigated by crush tests. In addition, the microstructure of these oxygen particles was studied to understand the relationship between the physical properties and the mechanical performance.

It was found that the granules are a promising shape for a packed bed reactor as no severe degradation in strength was noticed upon thermal cycling and creep testing. Especially, the addition of $Mn_2O_3$ to the ilmenite, which leads to the formation of an iron–manganese oxide, seems to results in stronger granules than the other ilmenite-based granules.



## 1. Introduction

Fossil fuel power plants are major emitters of greenhouse gases, which leads to an increase of $CO_2$ concentration in the atmosphere and as such, contribute to the global warming problem [1]. One possible method to reduce these $CO_2$ emissions is to capture the carbon, which can then be transported for use or storage [2–4]. There are different technologies available or currently under development which accomplish the capture of $CO_2$ from combustion sources, i.e. pre-combustion, post-combustion or oxyfuel combustion. Pre-combustion capture avoids production of $CO_2$ in combustion by transforming the carbon based component of the fuel to hydrogen which only produces water when burned. As such, $CO_2$ is separated before combustion when it is much more concentrated. Post-combustion capture tackles the problem by installing a separation process to treat flue gases, so no or only minor

* Corresponding author. Tel.: +32 14335719; fax: +32 14321186.
*E-mail address:* marijke.jacobs@vito.be (M. Jacobs).
1 Previously at VITO, Belgium.

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modifications are needed to the existing production processes. Nevertheless, post-combustion $CO_2$ capture systems have a significant impact on the energy production total costs [5]. On the other hand, oxy-combustion strongly increases the concentration of $CO_2$ in the flue gas by replacing air with oxygen for burning the fuel. Currently, the $CO_2$ capture technologies consist of very energy intensive steps, resulting in an increase in the cost of energy production and efficiency losses. In order to reduce energy losses, some authors are analysing methods and systems to combine powder production and $CO_2$ capture in a single step, as for example the fuel cell MCFC-based $CO_2$ capture system applied on small scale CHP plants [6].

One interesting capture route that is getting increased attention to overcome these disadvantages of the existing ones, is chemical looping combustion (CLC) [7–9]. This innovative technology combines power production and $CO_2$ capture in a single step and produces a pure $CO_2$ stream without any separation step or need of additional energy [10,11]. In this method, oxygen is transported from the air to the fuel via an oxygen carrier, which is based on a metal oxide. This oxygen exchange is carried out in cycles of two steps. During the first step, the fuel reacts with an oxygen carrier, a metal oxide (MeO), to form $CO_2$ and $H_2O$. This metal oxide is then reduced to a metal (Me) or a reduced form of MeO, so this first step is called the reduction step. In the second step, the oxygen carrier is oxidized with air. After this oxidation step, the regenerated material is ready to start a new cycle. The flue gas leaving the oxidation step contains $N_2$ and unreacted $O_2$. The exit gas during the reduction step contains only $CO_2$ and $H_2O$. After water condensation, almost pure $CO_2$ can be obtained.

There are different types of reactor configurations for chemical looping combustion, such as a fluidized bed or a packed bed reactor. The fluidized bed reactor concept is most often studied in literature [11]. For example, Mendiara et al. studied the behaviour of oxygen carriers based on bauxite waste in a 500 $W_{th}$ CLC unit. High combustion efficiencies (around 90%) were obtained in the fuel reactor with coal without agglomeration problems [12]. Even tests in larger fluidized bed installations have been performed. Mattisson et al. developed and tested calcium manganite oxygen carriers in a 10 kW and a 120 kW reactor [13]. Complete combustion was achieved in both reactors using these calcium based oxygen carriers, which were fabricated by spray drying. However, another interesting concept is the packed bed reactor, which has as main advantages an easy design and the possibility to work under pressure to have a higher efficiency compared to a fluidized bed concept, but the packed bed concept requires high temperature gas switching valves [14]. Kimball et al. confirmed that packed bed chemical looping combustion is a feasible configuration for $CO_2$ capture. The inherent separation of the $CO_2$ from the depleted air stream in a packed bed concept can even give a lower efficiency penalty than in fluidized beds [15]. In addition, Zhang et al. found a superior reactivity performance in fixed-bed mode compared to fluidized-bed mode, which resulted in higher values of $CO_2$ concentration and oxygen carrier conversion in pressurized chemical looping combustion of coal [16].

As oxygen carriers for chemical looping combustion, different ores and low cost materials such as ilmenite are recently being investigated [17,18]. The performance of ilmenite oxygen carriers in a 300 W CLC reactor were investigated by Moldenhauer et al. [19]. They reached $CO_2$ yield above 99% and noticed an increased reactivity of the oxygen carrier in the presence of sulfur. On the other hand, Mayer et al. determined the syngas conversion in a 10 $kW_{th}$ bubbling fluidized bed reactor for ilmenite particles, while Leion et al. investigated the reactivity of ilmenite oxygen carriers in a laboratory fluidized-bed reactor system [20,21]. The reactivity with both gaseous and solid fuels was also studied by Bidwe et al. They conducted a parametric study and found that ilmenite works well for the conversion of syngas when it is fully oxidized, but that reactivity reduces as ilmenite is reduced [22]. Besides testing in fluidized bed reactors, ilmenite was also tested in a packed bed reactor by Schwebel et al. [23]. The fixed bed reduction showed higher gas conversion by using coarser ilmenite particles than fluidized bed reduction, but some particle sintering occurred during oxidation. Furthermore, Cuadrat et al. studied the use of ilmenite as oxygen carrier for CLC of coal regarding the conversion of gaseous products from char gasification in a lab fluidized bed reactor [11]. In addition, they determined the porosity and the crushing strength of ilmenite particles in function of the amount of redox cycles [24]. As such, almost all studies deal with the reactivity of the oxygen carriers and the fuel conversion, but very few information is available on the mechanical properties of the oxygen carriers. Nevertheless, it is an important aspect since strong particles are needed in the reactor to assure a good chemical looping performance. Furthermore, there is almost no existing information on which type of microstructure is needed to obtain strong oxygen carriers. Therefore, in this study, the mechanical properties of ilmenite particles are investigated for their use as oxygen carriers in a packed bed CLC reactor. Particles in the shape of a granule with different compositions were subjected to thermal cycling, creep tests and crush tests in order to investigate the behaviour of these oxygen carriers under packed bed conditions. In addition, the microstructure of these oxygen particles was studied to understand the relationship between the physical properties and the mechanical performance.

## 2. Experimental

### 2.1. Materials

For a packed bed reactor, the ideal oxygen carrier material has a high activity through high and accessible surface area, a high selectivity and is resistant to poisoning. In addition, the structural integrity of the oxygen carrier is important for a good multi-cycle performance and a long service life [25]. An interesting naturally occurring material with proven performance in a fluidized bed reactor and with a low cost is ilmenite ($FeTiO_3$). Ilmenite is a mineral and it is mainly composed of $FeTiO_3$, with iron oxide as active phase. In order to avoid a large pressure drop in a packed bed reactor, larger oxygen carrier particles are needed such as granules. For this study, five different compositions based on ilmenite and an additive in the shape of granules were produced via extrusion by CTI. As additives, titanium oxide, manganese oxide, nanosized titanium oxide and bentonite were used [26]. The granules have a length of 7, 15 or 25 mm long with a diameter of 3–4 mm (Fig. 1). The compositions of the granules are given in Table 1.

### 2.2. Characterization

In order to study the microstructure of the different granules, SEM and XRD analysis were performed on granules G1, G4 and G5. XRD spectra were recorded on a Philips X'Pert diffractometer, while microscopic images and elemental analyses were carried out on the cross sections using a JEOL JSM-6340F field emission scanning electron microscope (FESEM) with an energy dispersive spectroscopy (EDS) system and using a FEI NOVA Nanosem 450. For these images, the granules were cut and embedded in epoxy resin, which is then cured at room temperature. Afterwards, these embedded granules were grinded and polished so that the different phases in the cross section are clearly visible. In addition, the pore size distribution of the granules was measured with mercury intrusion porosimetry (Pascal 140-240 series, Thermo Electron Corporation). In this technique, the pore size was calculated using

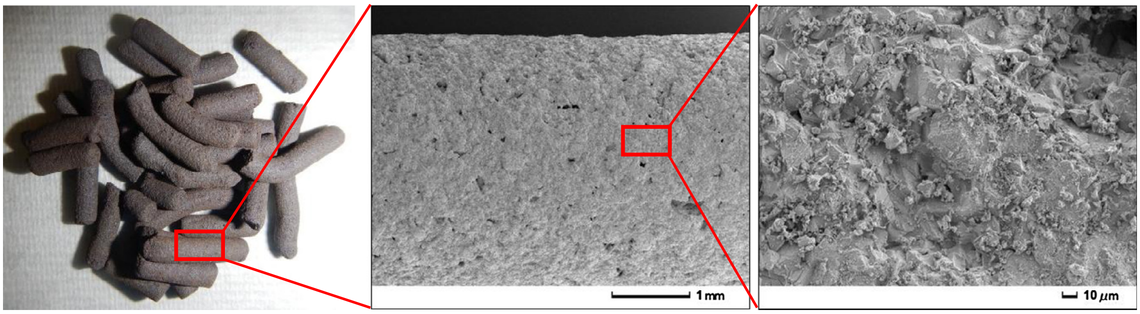


**Fig. 1.** Granules based on ilmenite after sintering at 1300 °C for 10 h (left), with a magnification of the surface (middle and right).

**Table 1**
The composition of different types of granules based on ilmenite.

| Sample | Composition |
|---|---|
| Granule G1 | 85% ilmenite–15% $TiO_2$ |
| Granule G2 | 85% ilmenite–15% $TiO_2$–0.5% nano |
| Granule G3 | 85% ilmenite–15% $TiO_2$–0.5% bentonite |
| Granule G4 | 90% ilmenite–10% $Mn_2O_3$ |
| Granule G5 | 75% ilmenite–25% $Mn_2O_3$ |

a contact angle of 140° and a surface tension of 480 Dynes/cm. The surface area of oxygen carriers was determined by Brunauer–Emmett–Teller (BET) method using a NOVA 3000-Series Quantachrome nitrogen adsorption analyser.

### 2.3. Mechanical testing

In a packed bed reactor, the oxygen carrier particles are subjected to severe conditions, such as pressure and temperature. If the particles are not able to withstand the reactor environment and disintegrate, the pressure drop in the reactor can increase, which will lead to a decrease of the reactor performance. Therefore, the thermal and mechanical behaviour of the oxygen carriers must be studied under these conditions.

#### 2.3.1. Creep test

To study the behaviour of the ilmenite particles under these severe reactor conditions, a setup to perform creep tests was built. During a creep test, a sample is placed under a constant load at a constant temperature. In the meantime, the deformation of the sample is recorded. Afterwards, the creep rate is calculated as the slope of this deformation curve in percent as a function of the time. As such, the creep rate is a function of the material properties, the exposure time and temperature and the applied structural load. The used setup is shown in Fig. 2 and it has a load range up to 1000 N and a maximum temperature of 1500 °C. The oxygen carrier is placed between two ceramic plates, so that the load is at its weakest point of the sample, i.e. laterally. The deformation is measured using $Al_2O_3$ rods connected to a linear variable differential transformer (LVDT), giving values for creep. The different types of granules have been tested under a load mimicking the actual load of a bed of 2.5 m column, taking into account a safety factor of 4 as is usual in this type of reactors.

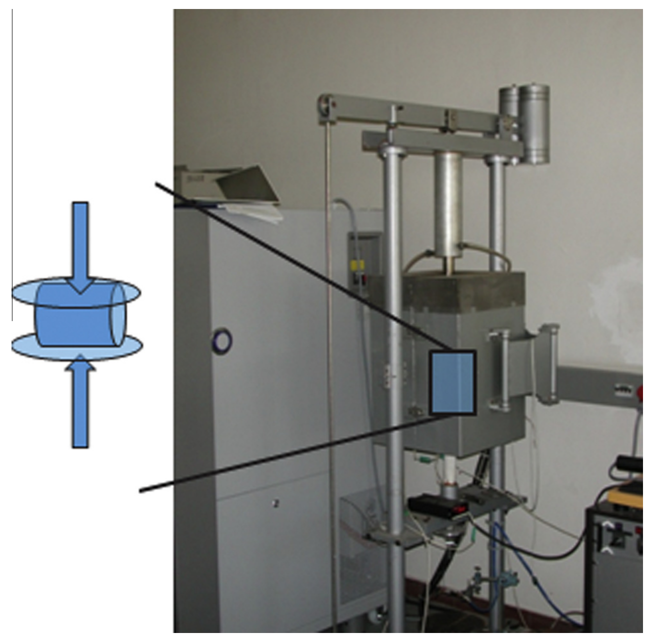

**Fig. 2.** The setup build for creep tests, together with a sketch of the sample positioning in the setup.

#### 2.3.2. Thermal cycling

A second set of tests was done in order to mimic the thermal cycling which the bed will undergo in the chemical looping process. The granules are put in and out a high temperature furnace, thereby undergoing thermal cycles from 600 °C up to 1200 °C with a holding time of 30 min and back. A picture of the setup and a thermal profile of a typical experiment are shown in Figs. 3 and 4. The granules with different compositions have been subjected to 50, 100 and 200 thermal cycles to evaluate the effect on the mechanical properties.

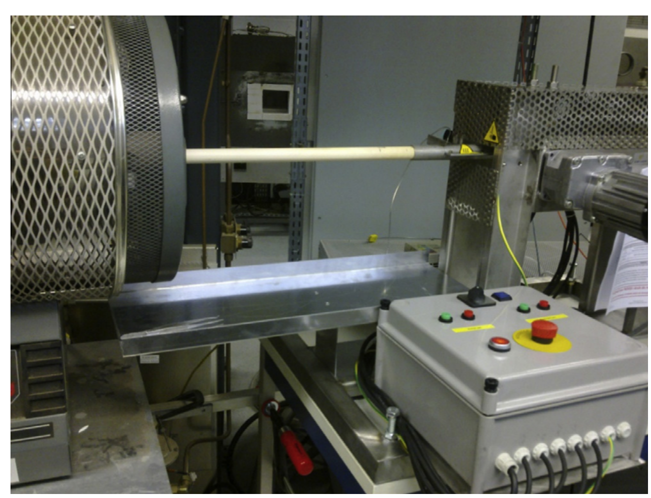

**Fig. 3.** The setup build for thermal cycling tests between 600 °C and 1200 °C.

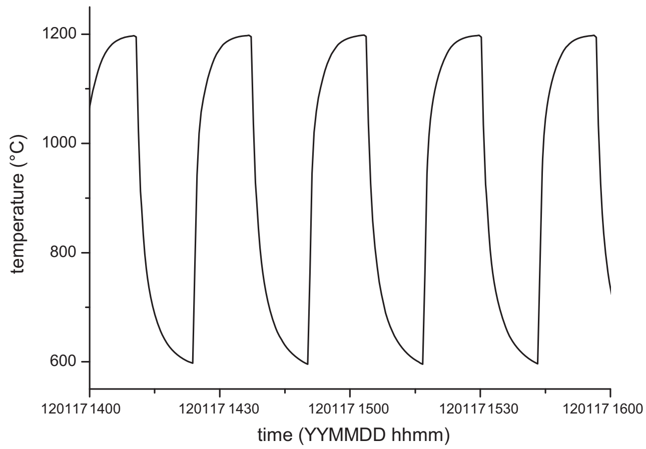


**Fig. 4.** The thermal profile in function of time of the thermal cycling tests.

*2.3.3. Crush test*

The individual particle crushing strength is also determined for the as-produced and tested material in order to know the resistance of the oxygen carriers to the severe conditions in a packed bed reactor. In such a columnar reactor a particle has to conserve its shape and mechanical integrity whatever its place in the reactor (bottom or top), to avoid heterogeneous reactions and exothermic points. The mechanical strength of the sintered oxygen carrier particles was assessed by measuring the force F (N) needed to break a single particle using an Instron 5582 Universal Testing Machine. The crushing strength is then calculated by dividing this force by the diameter of the granules. Then, this test is repeated on several samples to have an average crushing strength for each composition. As a target value for the crushing strength of the bed material, 2 DaN/mm is taken.

## 3. Results and discussion

SEM analysis was performed on the cross section of the granules with composition G1, G4 and G5 after embedding and polishing, together with EDS mappings. These are all shown in Figs. 5 and 6. In case of the $Mn_2O_3$-doped ilmenite granules, $Mn_2O_3$ particles (light grey in the image) are spread out in the ilmenite matrix (darker grey in the image) on the cross sections. The addition of 25% $Mn_2O_3$ gives a more homogeneously distribution of manganese oxide than the addition of 10%. The coarse ilmenite grains are well recognizable in the images. For the $TiO_2$-doped granule, a similar result is found; the titanium oxide is well distributed in the ilmenite matrix. However, the $TiO_2$ particles are much smaller than the $Mn_2O_3$ spots, so there are more difficult to see on a smaller magnification.

As the oxygen carrier extrudates are formed from ilmenite and titanium or manganese oxide raw powders, which are extruded and sintered at high temperature, an XRD diffraction pattern was recorded in order to verify the different phases that are formed upon sintering (Fig. 7). In case of the $TiO_2$-doped ilmenite, the ilmenite and the $TiO_2$ phase are clearly detected, but there seems to be

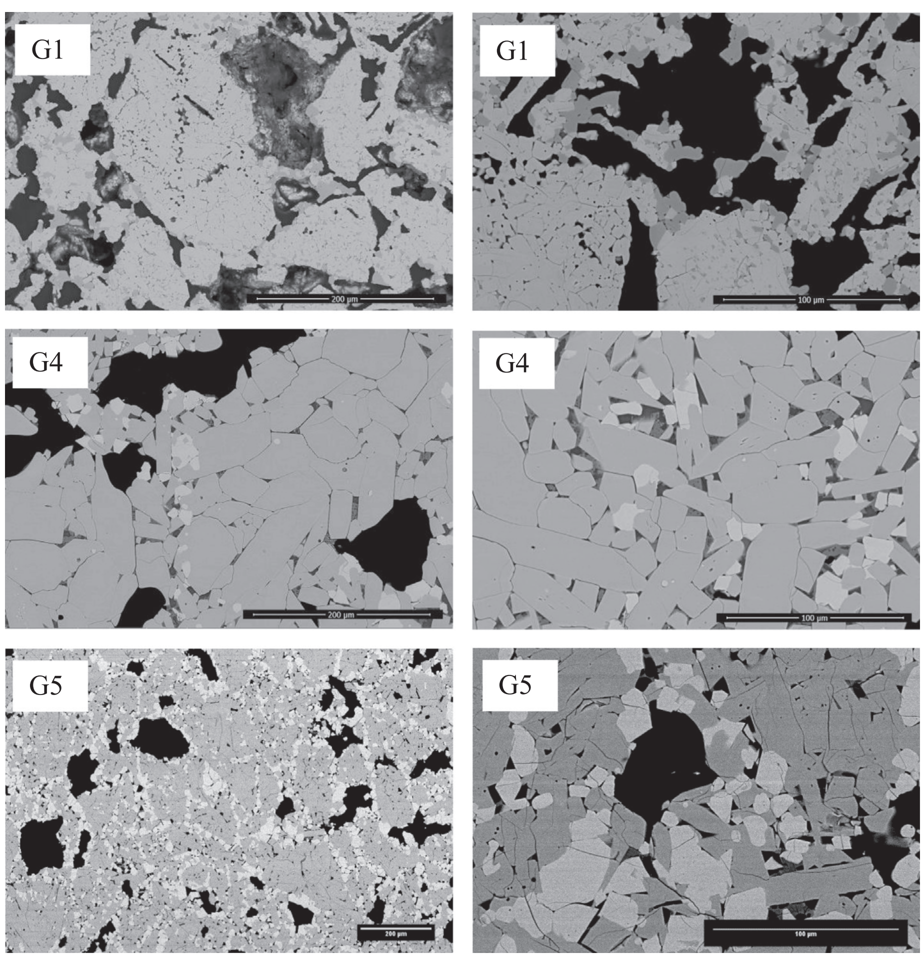


**Fig. 5.** SEM images of the cross sections of ilmenite based oxygen carrier extrudates with composition G1 (top), G4 (middle) and G5 (bottom).

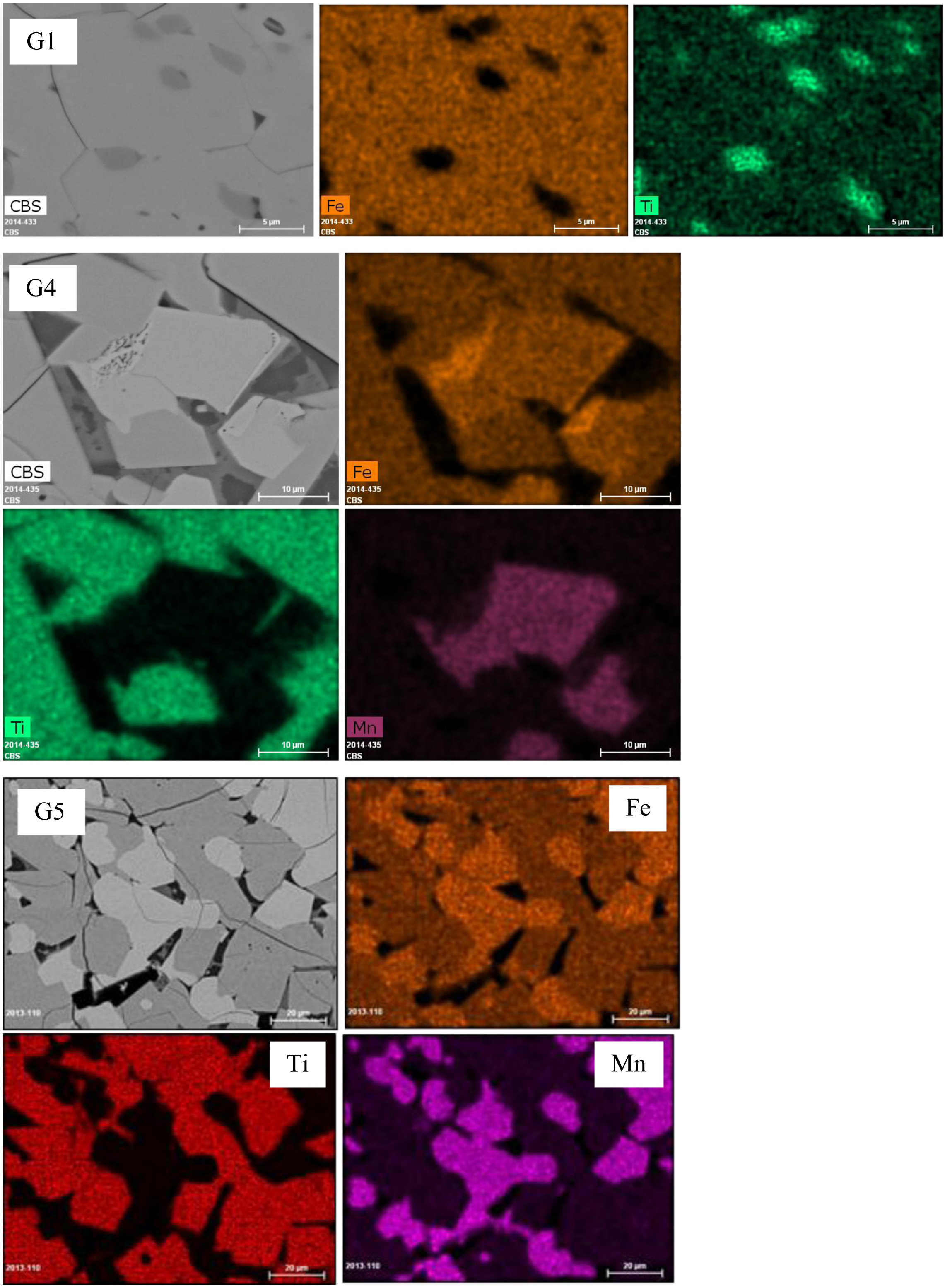


**Fig. 6.** EDS images of the cross sections of ilmenite based oxygen carrier extrudates with composition G1 (top), G4 (middle) and G5 (bottom).

almost no interaction between the two materials. However, when manganese oxide is used as a dopant, an iron–manganese mixed oxide is formed upon sintering due the reaction between the manganese oxide and the iron in the ilmenite phase. Depending of the amount of manganese oxide, around 10 to 15% of this iron–manganese oxide is formed.

Besides the microscopic and XRD analyses, the pore size distribution for all the granules was measured by mercury intrusion porosimetry, which is shown in Fig. 8. When 25% of manganese oxide is used as dopant for ilmenite, the largest amount of pores with a size below 0.5 µm can be noticed, while all the other granules have more or less the same amount of small pores. These types of granules have a total porosity between 24% and 31%, while the G5 composition has only a total porosity of about 15%. Another difference between the titanium and manganese doped ilmenite particles was identified by the BET analyses. The $TiO_2$-based ilmenite

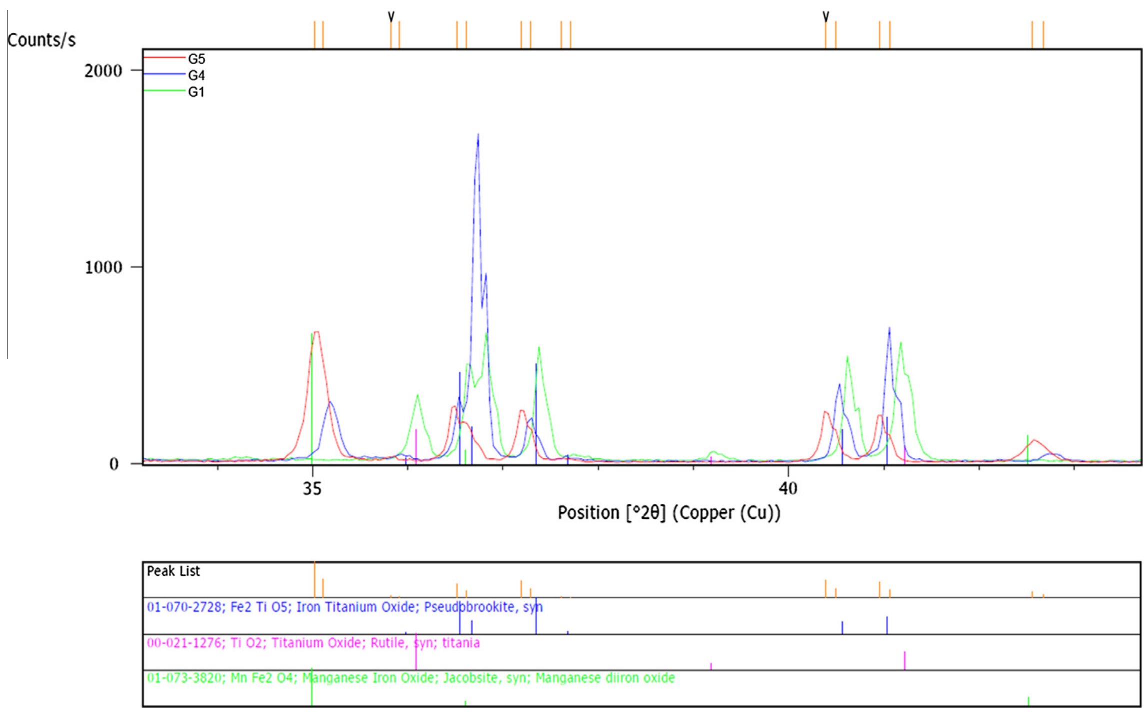


**Fig. 7.** XRD spectra of the G1 (green), G4 (blue) and G5 (red) oxygen carriers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

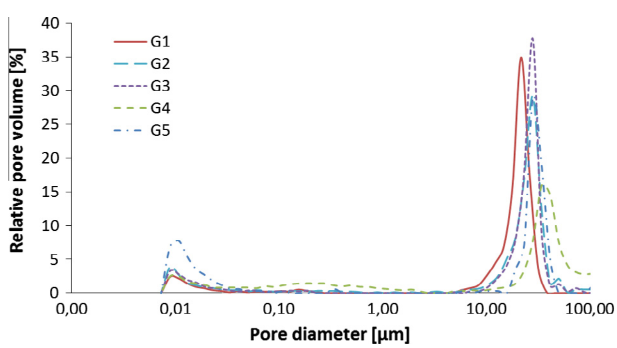


**Fig. 8.** The relative pore volume in function of the pore diameter for all the ilmenite based granules.

oxygen carriers have a specific surface area of about 1.9–2.3 $m^2\,g^{-1}$, while the $Mn_2O_3$-based oxygen carriers show a lower specific surface area, namely 1.0 $m^2\,g^{-1}$ or lower.

In view of the overall performance of the oxygen carrier material in a packed bed reactor, the mechanical properties of the pellets should be taken into account. The oxygen carrier material will be subject to severe conditions of temperature and pressure in the chemical looping process. The material has to cope with mechanical forces due to thermal and chemical expansion. It can be expected that these conditions will introduce changes to the structural, physical and chemical properties of the oxygen carrier structure. From a mechanical point of view, the material must be strong enough to support its own weight, also after several (thousands of) cycles. If the pellets disintegrate due to poor strength, the pressure drop over the bed will increase dramatically, jeopardizing the overall performance of the reactor. Also other problems can be expected, such as variations in heat flux, downstream fouling and so on. It is clear that the mechanical properties of a catalyst bed are mainly governed by those pellets with low strength, rather than all the pellets in the bed. This fact reveals that the low strength/probability part of the catalyst strength distribution is the critical domain for the mechanical reliability, rather than an average value. The mechanical strength of a catalyst pellet is distributed over a wide spread of values, which is an intrinsic property inherited from the brittleness of the materials. Mechanical failure is due to brittle fracture arising from a sudden catastrophic growth of a critical flaw under stress induced in the material bulk. The oxygen carrier pellets are porous and full of defects, crystal edges, dislocations and non-identical materials. Any discontinuation that appears in the oxygen carrier bulk may be treated as a flaw and hence origin of stress concentration. Variations in size, shape and orientation of these flaws result in the wide scatter of

**Table 2**
The crushing strength of the granules before and after thermal cycling tests.

| Sample | # cycles | Crush strength (DaN/mm) | Std dev. | Stdev (%) | Min CS (DaN/mm) | Max CS (DaN/mm) |
|---|---|---|---|---|---|---|
| Granule G1 | 0 | 6.76 | 1.7 | 25.1 | 4.85 | 9.93 |
| | 50 | 7.25 | 2.67 | 36.8 | 4.9 | 9.47 |
| | 100 | 6.72 | 2.28 | 33.9 | 4.66 | 12.2 |
| | 200 | 8.57 | 3.1 | 36.2 | 5.4 | 13.5 |
| Granule G3 | 0 | 7.33 | 1.67 | 22.8 | 4.76 | 9.76 |
| | 50 | 4.81 | 1.45 | 30.1 | 2.79 | 6.23 |
| | 100 | 5.1 | 1.57 | 30.8 | 3.04 | 7.59 |
| | 200 | 5.5 | 1.57 | 28.5 | 2.94 | 7.36 |
| Granule G4 | 0 | 10.2 | 3.14 | 30.8 | 5.84 | 17.05 |
| | 50 | 5.48 | 1.12 | 20.4 | 3.98 | 8.05 |
| | 100 | | | | | |
| | 200 | 3.34 | 1.1 | 32.93 | 1.42 | 5.12 |
| Granule G5 | 0 | 17.3 | 3.5 | 20.2 | 11.46 | 21.2 |
| | 50 | 9.67 | 3.82 | 39.5 | 4.5 | 17.9 |
| | 100 | | | | | |
| | 200 | 11.75 | 4.71 | 40.09 | 3.03 | 16.16 |

**Table 3**
The results of the creep tests on the ilmenite based granules.

| Sample | *T* (°C) | Creep rate (%/h) | Time to rupture (h) |
|---|---|---|---|
| Granule G1 | 1200 | 0.149 | >70 |
| | 1100 | 0.079 | >95 |
| | 1000 | 0.040 | >90 |
| | 600 | 0.010 | >95 |
| Granule G3 | 1200 | 0.116 | >70 |
| | 1100 | 0.082 | >168 |
| | 1000 | 0.053 | >70 |
| | 600 | 0.000 | >70 |
| Granule G4 | 1200 | 0.073 | >95 |
| Granule G5 | 1200 | 0.193 | >76 |

the strength data of the oxygen carrier pellets. In order to evaluate this, crushing tests, thermal cycling tests and creep tests were performed on all the different types of granules.

Before subjecting all the particles to thermal cycling or creep, the individual crushing strength of all the different granules was determined. All granule compositions made by CTI satisfy the criterion of at least 2 DaN/mm. After the thermal cycling tests with 50–200 cycles, the individual crushing strength of the granules was again measured. The results of these tests are summarized in Table 2. The granules do not undergo a severe mechanical deterioration upon cycling, as is clear from Table 2. There is no clear trend in the crushing strength data with cycling time, but the values of the crushing strength are all well above target value (i.e. 2 DaN/mm). Concerning the compositions of the oxygen carriers, the addition of bentonite gives no significant effect on the mechanical strength of the particles. Also the replacement of $TiO_2$ by $Mn_2O_3$ (G4) does not clearly improve the strength of the particles. On the other hand, a higher amount of $Mn_2O_3$ (G5) than G4 seems to give higher strengths, even after several thermal cycles. This could be due to the lower total porosity and the more homogeneous distribution of the manganese oxide phase in the granule.

Besides the thermal cycling tests, creep tests were performed as well on different types of granules. The results of these tests are given in Table 3. Although creep rates are higher with high temperatures, they do not become so severe that the particles fail, even at temperatures as high as 1200 °C. On the basis of these observations, the granules seem to be a promising shape for the oxygen carrier material in a packed bed chemical looping reactor. Contrary to the thermal cycling results, the G5 composition shows the highest creep rate at 1200 °C, while the composition with a small amount of additive, i.e. bentonite for the G3 composition, and the G4 composition with $Mn_2O_3$ show better performance during creep testing.

Oxygen carriers in a packed bed reactor do not only suffer from thermal variations in the reactor and the load of the packed bed, but they must also be able to take up and release oxygen during reactor operation. These constant (chemical) reactions of the material will induce structural changes. To simulate this chemical effect, the ilmenite granules were exposed to reducing-oxidation cycles in a fixed bed reactor at SINTEF and TU/e. The individual crushing strength of the granules was determined after 10, 20 and 50 redox cycles in order to study the evolution of the crushing strength. The results of these tests are summarized in Table 4. In addition, the porosity of the granules was measured by mercury intrusion porosimetry.

It is clearly observed that the granules undergo large structural changes, which is reflected in their porosity and mechanical crushing strength. The strength of the G1 granules after 50 redox cycles is well below the target strength, with weakest particles of 0.63 DaN/mm. It can be expected that granules with G1 composition in a packed bed chemical looping reactor will probably lead to fines formation. Furthermore, in most cases the porosity of the granules increases with higher amounts of redox cycles. The granules with composition G2 show a similar behaviour than the G1 granules. For G4 and G5, also deterioration is observed, but not so strongly as for G1 and G2. The crushing strength of these two compositions with $Mn_2O_3$ as additive remains above the target value (2 DaN/mm). For the tested compositions, G5 showed the best performance; it has the highest strength after 50 cycles. However, G4 undergoes a degradation of about 76% after 50 cycles, while there is 81% degradation for G5. As such, in relative terms, G4 performs slightly better than G5. The difference in behaviour between the $Mn_2O_3$-doped and the $TiO_2$-doped samples could be related to the smaller surface area and pore size of the $Mn_2O_3$-doped samples, which means that less reaction sites are available. This could lead to lower reaction rates and conversion for the G4 and G5 samples. Therefore, these aspects were monitored during the experiments. Despite the difference in microstructure, the conversion and reactivity were very similar for all the granules during reduction. There is only a minor difference between the two types of samples during oxidation.

As samples G1 and G2 already fail after 50 cycles and as samples G4 and G5 show a similar degradation behaviour than samples G1 and G2, it is very unlikely that samples G4 and G5 will survive 200 cycles (the maximum number of performed thermal cycles). They remained above the target value after 50 cycles since they had a higher strength in the beginning, but they will probably fail after about 70–80 cycles. As such, redox experiments up to 200 cycles were not performed.

After performing thermal cycling, creep and redox tests, the $Mn_2O_3$-doped samples have an overall better performance than the other samples. If $Mn_2O_3$ is used as an additive, an interaction occurs between ilmenite and the additive, while this is not the case if titanium oxide is used. The extra phase which is formed during interaction consists of about 10–15% iron–manganese oxide and this phase leads probably to the higher mechanical strength. However, it is unclear at the moment which amount of doping gives the strongest samples as none of the granules was overall superior to the others. A higher amount of $Mn_2O_3$ results in a stronger sample with a fine microscopic distribution of $Mn_2O_3$ compared to a small amount of $Mn_2O_3$. This microstructure seems to be beneficial for keeping mechanical strength during thermal cycling. On the other hand, during redox cycles it degrades relatively slightly more than the sample with less $Mn_2O_3$, but this difference is within error. However, during creep test the sample with

**Table 4**
The results of the crushing strength and the porosity of the granules after several redox reactions.

| Sample | # cycles | Crush strength (DaN/mm) | Std dev. | Stdev (%) | Min CS (DaN/mm) | Max CS (DaN/mm) | Poros. (Hg, %) |
|---|---|---|---|---|---|---|---|
| G1 | 0 | 9.26 | 1.94 | 20.9 | 6.34 | 12.90 | 29 |
| | 10 | 13.43 | 4.74 | 35.3 | 7.52 | 23.26 | 14 |
| | 20 | 4.83 | 1.28 | 26.5 | 3.45 | 7.38 | 23 |
| | 50 | 1.18 | 0.44 | 37.3 | 0.63 | 1.79 | 32 |
| G2 | 0 | 6.14 | 1.46 | 23.7 | 4.38 | 8.92 | 27 |
| | 10 | 8.06 | 2.77 | 34.4 | 5.30 | 14.70 | 17 |
| | 20 | 2.41 | 0.85 | 35.3 | 1.73 | 4.63 | 26 |
| | 50 | 0.57 | 0.28 | 49.1 | 0.29 | 1.17 | 26 |
| G4 | 0 | 10.1 | 3.14 | 31.09 | 5.84 | 17.05 | 21 |
| | 10 | 16.16 | 6.3 | 38.99 | 6.13 | 27.02 | 30 |
| | 20 | 5.24 | 2.43 | 46.37 | 3.00 | 11.25 | 28 |
| | 50 | 2.47 | 0.76 | 30.77 | 1.74 | 4.16 | 30 |
| G5 | 0 | 17.2 | 3.2 | 18.60 | 11.46 | 21.20 | 15 |
| | 10 | 14.85 | 4.17 | 28.08 | 9.66 | 24.86 | 17 |
| | 20 | 6.94 | 2.78 | 40.06 | 2.74 | 12.15 | 22 |
| | 50 | 3.26 | 2.35 | 72.09 | 0.65 | 4.26 | 29 |

the highest amount of $Mn_2O_3$ undergoes more deformation than the sample with only a small amount of $Mn_2O_3$. As such, it seems that $Mn_2O_3$ softens the sample at high temperature. As long as there is no load on the sample (as during thermal cycling), this softening is no problem. Since creep resistance is very important in a packed bed reactor, the higher amount of $Mn_2O_3$ could give problems in the reactor.

## 4. Conclusions

Granules produced by CTI have all acceptable mechanical strength as produced. During creep testing, the granules were able to withstand load, even at 1200 °C. In case of thermal cycling tests between 600 °C and 1200 °C, the granules show no clear trend after several thermal cycles, but their mechanical strength is still well above the critical value. As such, it is clear from the mechanical and thermal testing that the granule shape is a promising shape for oxygen carrier particles in a packed bed reactor. Regarding the different compositions, the small addition of nano $TiO_2$ or bentonite to ilmenite has no strong influence on the mechanical behaviour of the granules. On the other hand, the addition of $Mn_2O_3$ leads to the formation of smaller pores and an extra iron–manganese oxide phase, which seems to give oxygen carriers that are more able to withstand the reactor conditions in a packed bed reactor for chemical looping combustion.

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