

Fig. 11. Microtomographic appearance of medium pellet before and after direct reduction at 1000 °C for 90 min in (a-a3) unreduced state, and (b-b3) reduced state; (a1-a3 and b1-b3)cross-sections of the porosity evolution of the investigated pellets in the directions (a1,b1) X, (a2,b2)Y and (a3,b3)Z.

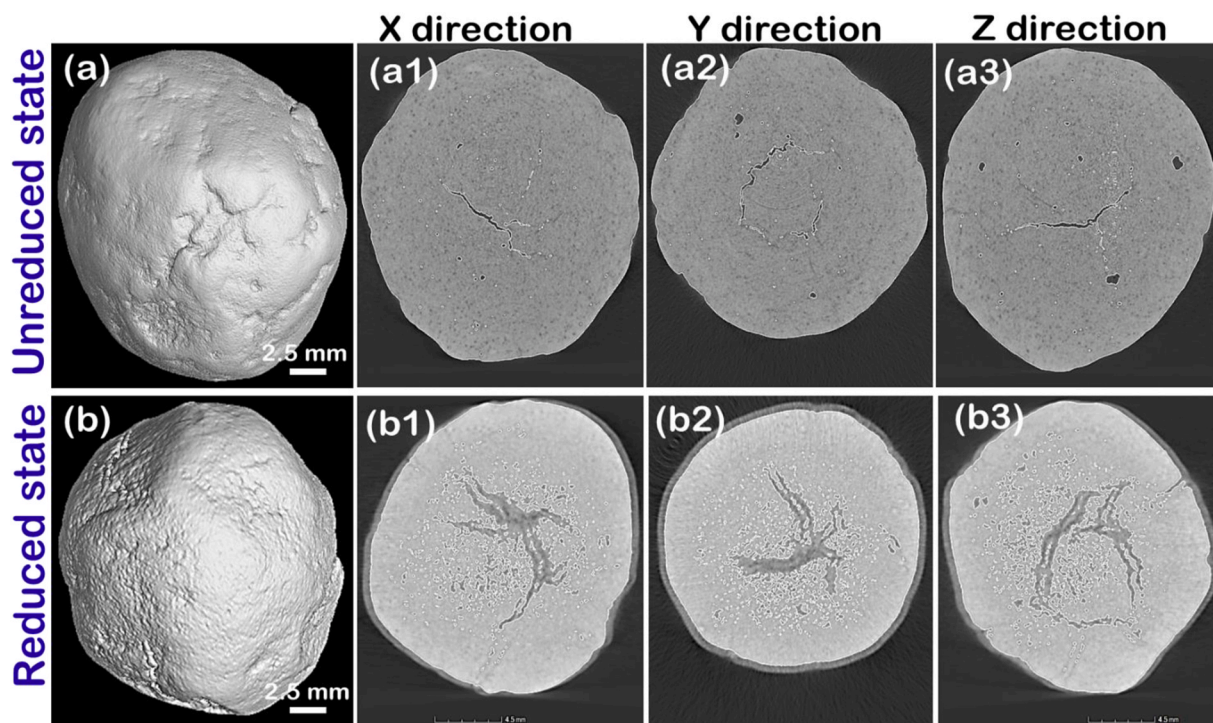


Fig. 12. Microtomographic appearance of big pellet before and after direct reduction at 1000 °C for 90 min in (a-a3) unreduced state, and (b-b3) reduced state; (a1-a3 and b1-b3)cross-sections of the porosity evolution of the investigated pellets in the directions (a1,b1) X, (a2,b2)Y and (a3,b3)Z.

structure.

Figs. 13 and 14 show the changes in pore properties and the evolution over time of a small pellet subjected to direct reduction at 950 °C and 1000 °C respectively. Fig. 13 (a) shows the pellet after 5 min. The pores are small and well distributed throughout the material. These pores are probably due to the original microstructure of the pellet before

the reduction process started. Fig. 13(b) after 30 min shows a slight increase in pore size and some cases where the pores start to merge, indicating the onset of microstructural changes even in the unreduced state, possibly due to thermal effects. After 90 min, as can be seen in Fig. 13 (c), some pores have merged to form larger and more complex structures, indicating that even without reduction, prolonged exposure

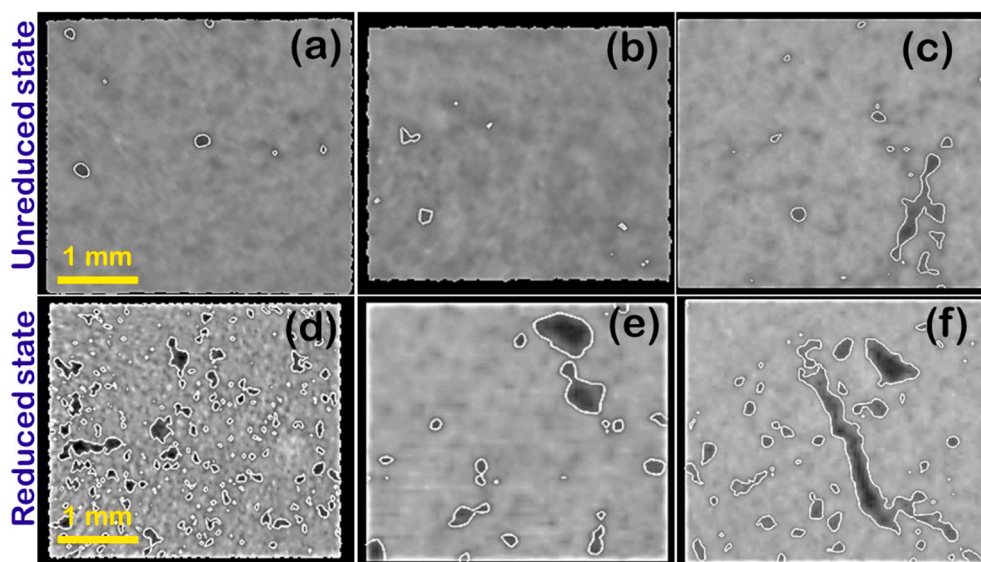


Fig. 13. Pores aspects and evolution as function of reduction time for the small pellet before and after direct reduction at 950 °C for (a,d)5 min, (b,e) 30 min, and (c, f) 90 min.

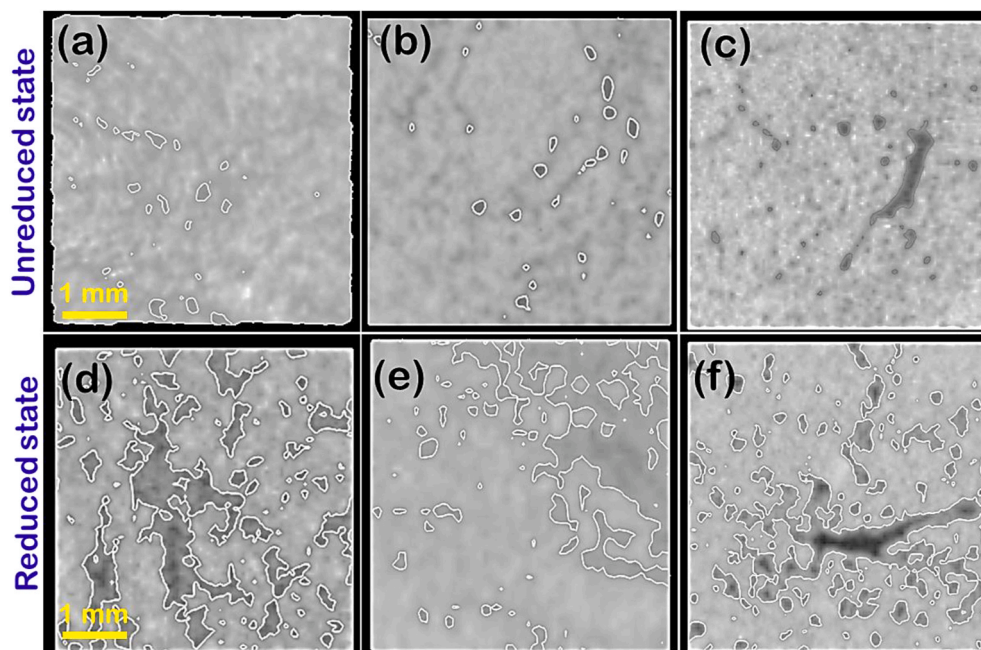


Fig. 14. Pores aspects and evolution as function of reduction time for the small pellet before and after direct reduction at 1000 °C for (a,d)5 min, (b,e) 30 min, and (c, f) 90 min.

to high temperatures can promote microstructural evolution. After 5 min of reduction, Fig. 13 (d) shows a clear contrast to the unreduced state. The pellet exhibits a high pore density, many of which are larger and more irregularly shaped, indicating a rapid change in porosity as a result of the reduction process. After 30 min, Fig. 13 (e) shows further growth and coalescence of the pores. The pore shapes are more diverse and the boundaries between the pores are less pronounced, reflecting the ongoing effects of reduction. After 60 min of reduction, Fig. 13 (f) shows extensive coalescence of the pores, resulting in large interconnected pore structures. This shows the peak of the microstructural changes caused by the reduction, with both the size and interconnectedness of the pores having changed significantly. Fig. 14(a) after 5 min shows sparse, small pores. After 30 min, as shown in Fig. 14(b), the pores appear slightly larger, indicating thermal effects, although no reduction

has taken place. After 90 min (see Fig. 14(c)), the onset of pore growth and coalescence can be observed, a trend that continues over time even before reduction.

After 5 min of reduction, as shown in Fig. 14 (d), the pellet shows a clear increase in porosity with larger and better cross-linked pores. After 30 min (see Fig. 14 (e)), the pores have grown further and have formed a more interconnected network, a sign of progressive microstructural evolution due to the reduction. Finally, Fig. 14 (f) shows that after 90 min, the pellet exhibits extensive fusion of the pores, resulting in large interconnected channels, indicating significant structural changes. Fig. 15 shows the microtomographic appearance of the pores in small, medium and large pellets after direct reduction for 30 min at two different temperatures: 950 °C and 1000 °C. It is obvious that at 950 °C, as shown in Fig. 15 (a), the small pellet has small, well-defined pores

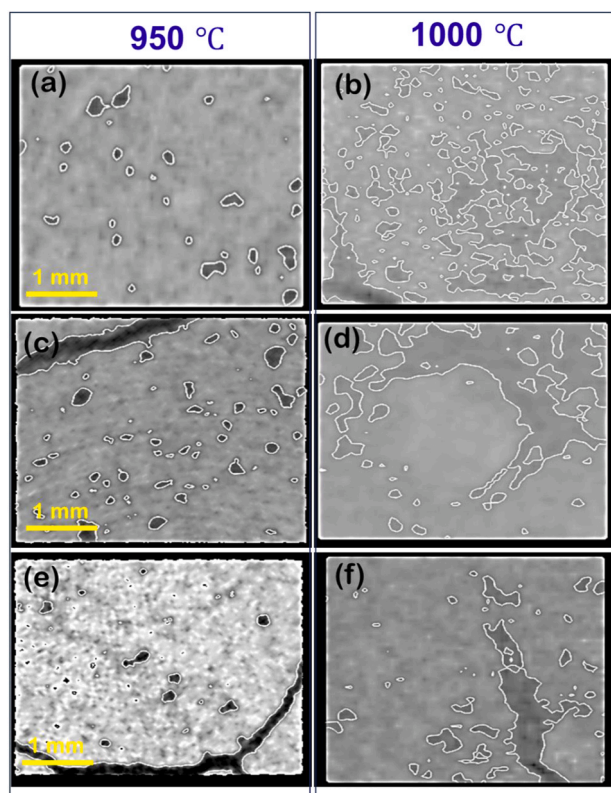


Fig. 15. Pores aspects and evolution as function of pellet size after direct reduction for 30 min, (a,b) small, (c,d) medium, (e,f)big.

with a slight coalescence. In contrast, at 1000 °C, as seen in Fig. 15 (b), the pores are much more numerous, larger and interconnected, indicating a more pronounced porosity evolution due to the higher temperature.

At 950 °C, the medium pellet shows larger pores compared to the small pellet at the same temperature, with some pores merging together (see Fig. 15 (c)). At 1000 °C, as seen in Fig. 15 (d), the porosity is significantly increased, with extensive coalescence and larger interconnected pore networks. At 950 °C (see Fig. 15 (e)), the large pellets have a slightly larger pore distribution than the small and medium pellets, with a relatively heterogeneous pore distribution. Even at 1000 °C, as shown in Fig. 15 (f), the porosity appears similar to the medium pellet, with large interconnected pores, although the overall porosity appears lower compared to the medium pellet at the same temperature. Tortuosity is an important factor in the discussion of porosity development in HyDR, as it can significantly affect the transport properties within the pellet, such as diffusivity and permeability. In this context, all microtomographs show greater porosity and cross-linking of the pores at 1000 °C compared to 950 °C. Although this indicates an increased permeability due to larger pores, the complexity of the pore network, namely the tortuosity, can also increase. A high tortuosity means that the path for the gas to diffuse through the pellet is more tortuous and complex, which could slow down the reduction process despite the increased porosity. In addition, the microtomographs show that the smaller pellets tend to have a faster development of porosity with a higher rate of interconnected pore formation, especially at 1000 °C. This may result in higher tortuosity as the smaller volume of the pellet may restrict the growth and direction of the pore channels, resulting in a more tortuous path. Larger pellets could have a more uniform pore distribution with potentially lower tortuosity. The peak in porosity rate indicates a point where porosity increases most rapidly, which could be associated with a period where tortuosity also develops rapidly. After the peak, the reduction in porosity rate could be

influenced by the increase in tortuosity, which hinders the further development of porosity as it is difficult to remove additional material without extensive new pore formation.

Fig. 16 shows the calculated change in porosity as a function of time during HyDR at two different temperatures. Across all pellet sizes, an increase in porosity with time can be observed at both temperatures. It is notable that porosity increases rapidly at 1000 °C for each pellet size before reaching a peak and then decreasing. This trend is particularly pronounced and occurs earlier compared to 950 °C. At 950 °C, as shown in Fig. 16(a), the porosity of the small pellets increases steadily over time, surpassing the porosity values of the medium and large pellets. This behaviour highlights the fact that smaller pellets, with their larger surface area relative to volume, are likely to undergo more efficient gas-solid interactions, allowing for a faster increase in porosity. Conversely, the medium and large pellets show a more gradual increase in porosity, with the large pellets showing the most significant overall increase at the end of the reduction time. Looking at the results at 1000 °C (see Fig. 16 (b)), there is a sharp increase in porosity for all pellet sizes, reaching a maximum faster than at the lower temperature. This peak value, followed by a decrease in porosity, indicates an increased reaction rate at the higher temperature. The earlier onset of porosity stabilisation or reduction at 1000 °C could be due to accelerated reduction kinetics driving the transition to the sintering phases, or to material consumption subsequently preventing further porosity development.

Fig. 17 provides contour maps at three time points (10, 30, and 90 min) that illustrate the porosity distribution within each pellet, with warmer colors indicating higher porosity and cooler colors indicating lower porosity. For the small pellets in Fig. 17(a), at both temperatures, the porosity is initially concentrated in certain regions and becomes more uniform over time. At 1000 °C, the porosity increases more rapidly and to a greater extent than at 950 °C, covering a larger area of the pellet. For medium pellets given in Fig. 17 (b), a similar pattern is seen with porosity developing and spreading over time. Again, the porosity at 1000 °C is more extensive than at 950 °C, particularly at the 30 and 90-min marks. Lastly, the big pellets in Fig. 17(c) demonstrates the porosity changes are less pronounced at 950 °C, with some regions showing minimal porosity even after 90 min. At 1000 °C, the increase in porosity is more noticeable, but the distribution is uneven, with some areas experiencing significant porosity while others remain relatively unchanged.

When the temperature is increased to 1000 °C, the microstructure in both the small and big pellets shows a significant increase in porosity, as can be seen in Fig. 18 (c) and (d). The small pellet at 1000 °C (c) exhibits larger voids compared to its counterpart at 950 °C (a), suggesting that temperature plays a significant role in the development of porosity, which is confirmed by the increased overall rates of porosity development at 1000 °C in Table 6. The bigger pellet at 1000 °C (Fig. 18 (d)) shows even more extensive pore formation, which is consistent with the trend of increased porosity at larger pellet size and higher temperatures.

The presence of iron is widespread and intense throughout the mapping, indicating a significant degree of reduction (Figs. 19 and 20). The silicon map shown in Fig. 20 highlights concentrated areas of silicon that are more pronounced than in the mapping of the small pellet from Fig. 19. This is attributed to the larger pellet size affecting the aggregation of silicon compounds, possibly due to slower reduction kinetics in the core of the pellet compared to its surface. In particular, Fig. 20 shows that calcium is present throughout the pellet, suggesting the presence of calcium in the gangue material. This uniform presence of calcium could also influence the reduction behavior and final microstructure of the pellet. Aluminum is sparsely distributed, similar to the findings in the small pellet, but is less concentrated in the large pellet. This could be due to the size of the pellet and the resulting influence on the distribution of non-ferrous elements during pellet formation and reduction. The oxygen map shows a significant number of white dots, indicating that oxygen is still present in the pellet. The distribution is not entirely uniform, which, when correlated with the porosity observed in the SEM image, suggests

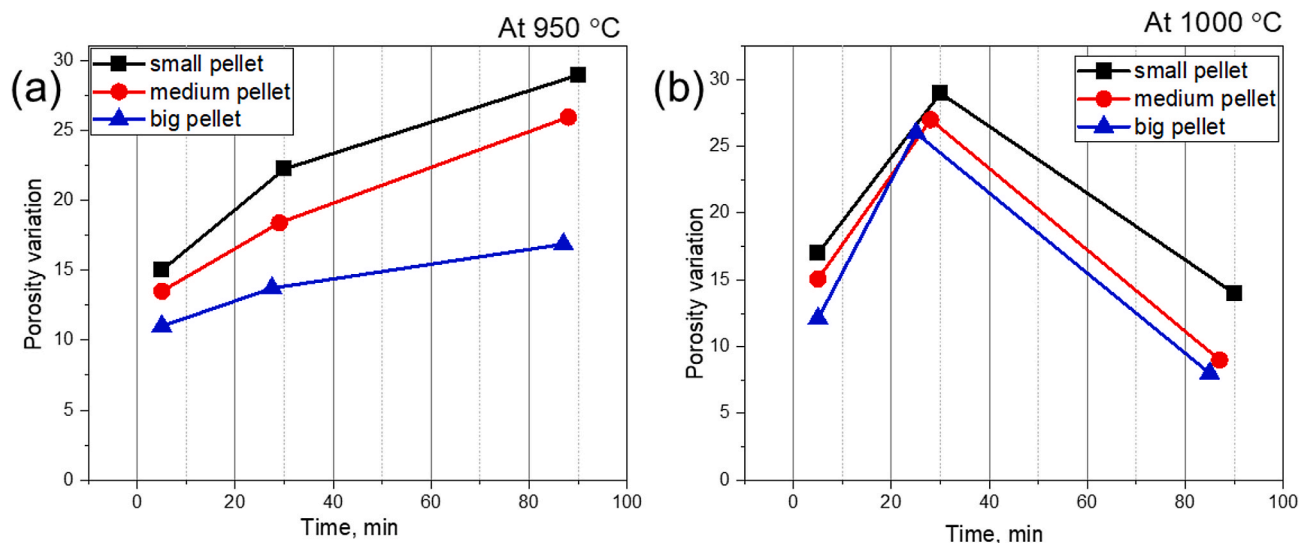


Fig. 16. The calculated porosity variation evolution over reduction time during HyDR at (a) 950 °C (b) 1000 °C.

that oxygen may be more abundant in areas of less void formation.

5. Discussion

In the direct reduction of iron oxide with hydrogen, the first two stages, i.e. the reduction of H to M and the reduction of M to W, are mainly controlled by the chemical reactions at the interfaces. In the third stage of reduction, i.e. the reduction of W to Fe, processes based on atomic diffusion are leading and suppress the reduction process [55,57]. For this reason, the morphology and physical properties of the pellets play an important role in creating the diffusion pathways at this stage. In this regard, the mass change during each process can have a significant impact on the formation and development of the type of pores, which in turn can influence the regeneration rate in each step of the reaction by providing an effective surface area that influences chemical reactions. Considering that porosity leads to a larger active surface area available for the chemical reactions in the first two stages of the reduction process, the development of porosity can lead to a larger contact area between hydrogen and iron oxides, which in turn leads to an increase in the reduction reaction rate in the first two stages of the process. However, in the third stage, atomic diffusion, which depends on the penetration of the material mass, can be influenced to a certain extent by porosity, so that the development of porosity can increase atomic penetration to a certain extent.

When comparing the results for different pellet sizes at 950 °C and 1000 °C, it can be seen that the higher temperature significantly increases the effects on porosity evolution and cracking for all pellet sizes, as shown in Fig. 21 (a) and (b).

In the simulated results shown in Fig. 21, small pellets show a more pronounced increase in porosity variation at both 950 °C and 1000 °C compared to medium and large pellets. Also, it is obvious that in all three pellet sizes, the porosity variation increases more rapidly at the higher temperature of 1000 °C compared to 950 °C (Fig. 22). This observed behaviour is consistent with the theoretical prediction and microtomographies images, which support the notion that smaller pellets, with their larger surface area relative to volume, allow for more effective gas-solid interactions and thus promote a faster reduction process. In addition, the simulation results show that for all pellet sizes, porosity variations are greater at 1000 °C than at 950 °C. This trend is consistent with the higher reaction rates at higher temperatures, as can be seen in Fig. 6 and Table 5. At 950 °C, the porosity variation increases gradually for small and medium pellets until it reaches a plateau at around 70 and 72 min respectively. In contrast, large pellets show a stronger increase in

porosity variation and do not reach a plateau within the observed time period. At 1000 °C, the porosity variation increases rapidly for all pellet sizes and peaks at around 63, 64 and 66 min for small, medium and large pellets respectively. After these peaks, the porosity variation decreases slightly, possibly due to sintering or similar processes that reduce porosity at higher temperatures. In addition, the increase in temperature and porosity likely leads to increased diffusion coefficients, which explains the larger porosity variations observed at 1000 °C. The trends observed in the simulations reflect the known effects of pellet size and temperature on the HyDR process. Due to their larger surface area relative to volume, smaller pellets respond faster and reach higher porosity variations earlier than their larger counterparts. The modest decrease in porosity variation after peaking at 1000 °C indicates the presence of a compensating mechanism, possibly sintering, which becomes more important at higher temperatures and longer reaction times. The simulation results emphasize the importance of pellet size and temperature in the HyDR process. They confirm that smaller pellets exhibit larger porosity variations and higher temperatures contribute to increased porosity, although they can also lead to complex effects such as sintering in the later stages of reduction.

In addition, the calculated developments of the porosity variations agree with the contour maps. The smaller pellets reach higher porosity levels faster, indicating their faster response to the HyDR process. This can be explained by the fact that smaller pellets, with their larger surface area relative to volume, are more reactive, allowing the reducing gas to penetrate and react more thoroughly, resulting in higher porosity. With larger pellets, on the other hand, the lower surface area to volume ratio leads to slower reaction kinetics, so that the porosity develops more slowly and less uniformly, as can be seen in the contour maps for the big pellets at both temperatures. The pronounced increase in porosity and the increased cracking observed at 1000 °C are scientifically associated with the accelerated kinetics of diffusion and reaction processes due to the higher temperature, which intensifies pore growth and coalescence as well as cracking caused by thermal stresses. This is particularly noticeable in larger pellets at 950 °C, where the tendency for larger pores may be a result of their larger volume and the resulting internal stresses and structural changes. However, at 1000 °C, the differences in porosity between pellet sizes are less pronounced, suggesting that the influence of increased temperature on the reduction process outweighs the effects of pellet size, with increased reaction rates and atomic mobility contributing to a more uniform porosity development between the different sizes. From the microtomographs at 950 °C compared to 1000 °C, it can be interpreted that higher temperatures lead to greater