

Fig. 17. The simulated results for the time-dependent change in porosity during HyDR at 950 °C and 1000 °C for 90 min for different pellet sizes (a) small, (b) medium and (c) big.

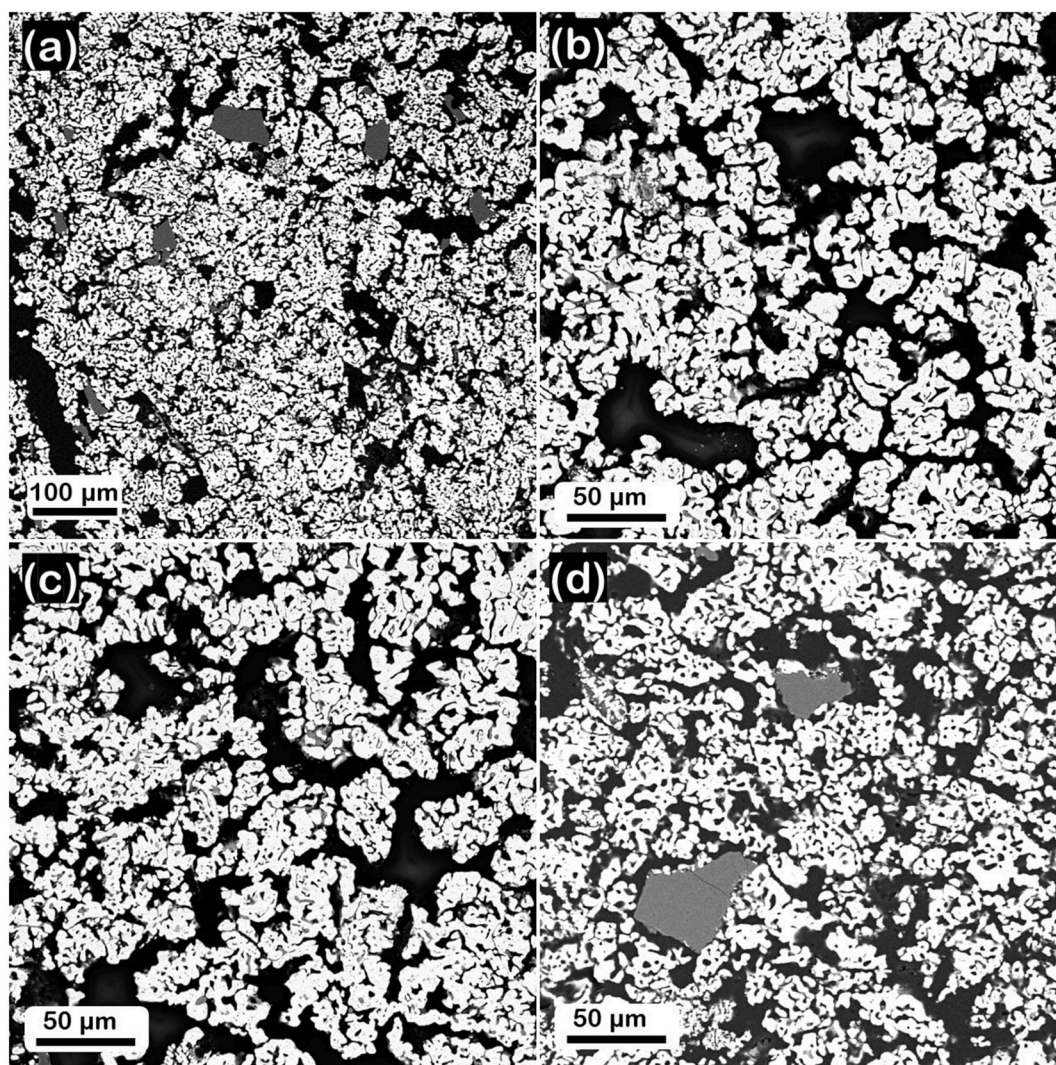


Fig. 18. SEM images showing the microstructure of reduced pellets at two different temperatures: (a, b) 950 °C and (b) 1000 °C for 90 min. In (a, c) a small pellet is shown, while (c, d) shows a larger pellet.

Table 6

Calculated porosity rate for intermediate and total reduction reactions for different pellet size at 950 °C and 1000 °C.

Temp. °C	Pellet	Porosity evolution rate			Total porosity evolution rate
		H → M	M → W	W → Fe	
950	small	3.13	4.76	0.28	8.17
	medium	5.74	4.14	0.22	10.1
	big	7.03	9.22	0.60	16.85
1000	small	4.50	4.81	1.00	10.31
	medium	4.13	5.26	1.20	10.59
	big	8.56	13.72	2.61	24.89

porosity and cracking. In addition, the rate at which porosity develops can be visually correlated with the extent and size of the pores in the microtomography images. For example, the microtomography images at 1000 °C showed a rapid development of large interconnected pores, which is consistent with the higher porosity rates at this temperature. In addition, the size of the pellets influenced the rate of porosity development, with smaller pellets showing a more pronounced rate of porosity increase at 1000 °C than medium and large pellets. This is consistent with the microtomographic images, where smaller pellets

showed rapid changes, especially at higher temperatures. Furthermore, the time to reach the maximum porosity rate corresponds to the images where the strongest pore coalescence was observed. For example, at around 30 min, the microtomographs showed remarkable pore growth and connectivity, which is consistent with the peak values in Fig. 16. Comparison of the calculated porosity rate for the intermediate stages given in Table 6 shows that the rate of porosity development near the pellet surface is relatively high, so the tortuosity of the pores near the pellet surface is usually quite high. This results in a lower effective diffusion coefficient, which leads to a slow reduction rate, especially from W to Fe, in the late stages of HyDR. To justify these observations, an understanding of the kinetic behaviour of the reduction reactions during the HyDR process is required. The increased porosity rates at 1000 °C compared to 950 °C are due to the greater kinetic energy promoting the diffusion and reduction reactions. The temperature dependence of reduction kinetics means that higher temperatures accelerate reaction rates, leading to faster and more extensive microstructural changes, including the formation and expansion of pores. In addition, the observed decrease in porosity rate over time is explained by the depletion of the reducible material and the increasing difficulty of gas diffusion as larger pores develop, as well as possible sintering or restructuring of the pellet at higher temperatures, which can prevent further increases in porosity. The greater temperature gradient at 1000 °C could also cause a thermal shock that further intensifies crack development,

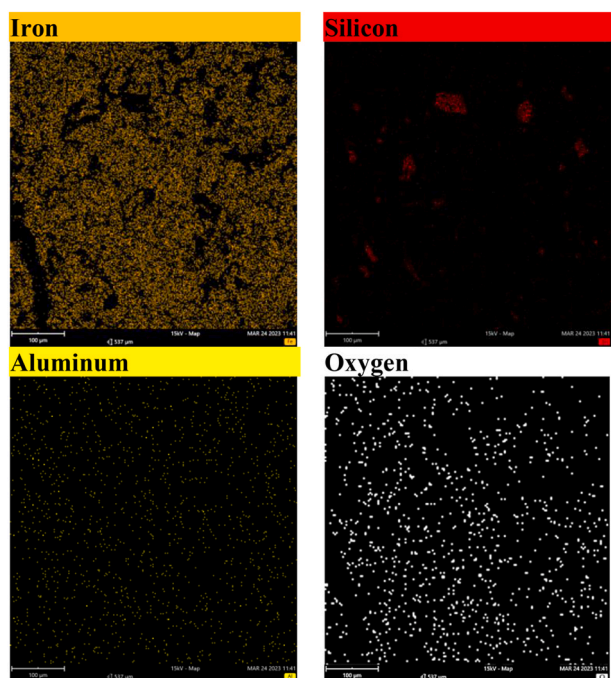


Fig. 19. Composition mapping of the small pellet reduced for 90 min at 950 °C (Fig. 18 (a) shows a corresponding SEM image).

suggesting that higher temperatures generally accelerate microstructural changes in materials that are thermally treated.

During HyDR, the reduction rate varies with time, assuming that the diffusion of H_2 to or H_2O from the pellet/gas interface is the rate-limiting step of the reaction [1]. This can be attributed to a continuously increasing specific surface area of the pellet and the corresponding change in gas permeability. However, the reduction rate of the intermediate reactions over the entire HyDR shows a relatively stable reduction rate for all pellet sizes within the reduction degree range of ~ 0.56 – ~ 7.2 for 950 °C and ~ 2.54 to ~ 5.39 for 1000 °C. It is important to note that at lower reduction temperatures, 950 °C in this case, the reduction rate ranges from ~ 0.33 to ~ 0.7 , especially for small pellet sizes, as reported in Ref. [1]. For most of the reduction rates calculated in the present work, the reduction rates are an order of magnitude higher than those reported in the literature [1,19]. This can be attributed to several reasons, such as a higher reduction temperature and a higher porosity content in both the unreduced and reduced states. In particular, the high porosity and tortuosity, i.e. the degree of percolation topology of the inner free surface areas, provide fast diffusion pathways for the reactants and abundant potential nucleation sites. The accessibility of the inner surfaces to the reducing gas significantly accelerates the global reduction kinetics. It also plays an essential role in the uptake and removal of the oxidation product, i.e. the water produced during the redox reaction.

Table 6 shows that the porosity evolution rate is positively correlated with the pellet size across both temperatures and reduction stages. In particular, small pellets at 950 °C show the lowest porosity evolution rate during the transition from H to M, while big pellets show the highest rates. This trend also applies to the subsequent stages of reduction, with big pellets showing the most significant increase in the overall porosity evolution rate. At the elevated temperature of 1000 °C, it again can be seen a reinforcement of this pattern, with porosity rates for equivalent sizes exceeding those at 950 °C, suggesting that higher temperatures promote porosity evolution. In particular, during the final reduction step from W to Fe, the porosity evolution rate increases dramatically, especially for big pellets.

As seen from Table 6, the small pellets show a higher porosity

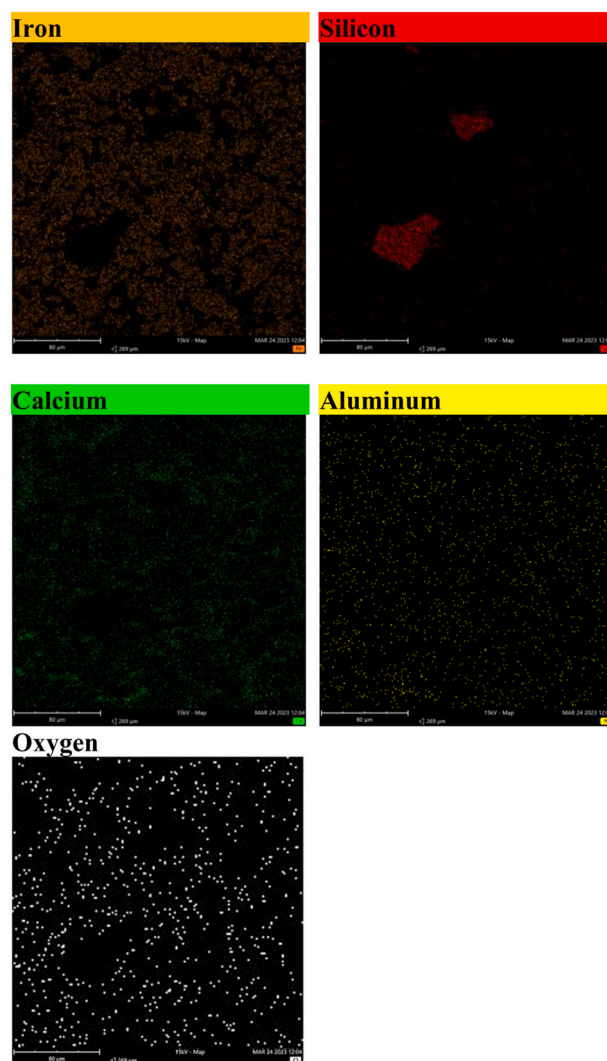


Fig. 20. Composition mapping of the big pellet reduced for 90 min at 950 °C (Fig. 18 (d) shows a corresponding SEM image).

evolution rate (4.76) during the M to W phase than the medium (4.14) and big pellets (9.22). This could be due to the smaller pellets having more surface curvature, which could increase surface reactivity and allow for faster reduction kinetics, although the overall trend is less clear and could be influenced by other factors such as gas diffusion dynamics. The curvature effect can be an important factor in the HyDR of iron oxide pellets and influence the reduction kinetics and porosity evolution [58]. In the final stages of W-to-Fe reduction at 950 °C, porosity rates are significantly lower in all sizes, suggesting that the curvature effect is less effective in the final stages of reduction, possibly due to the slowing of reaction kinetics as the reduction nears completion. At 1000 °C, porosity evolution rates generally increase for all pellet sizes, suggesting that higher temperatures mitigate the curvature effect by improving reduction kinetics throughout the pellet and not just at the surface. For big pellets, the porosity evolution rate jumps significantly from H to M to 8.56, indicating that temperature can enhance the curvature effect for larger pellets, possibly due to better heat transfer and reaction rate. The M to W stage at 1000 °C shows increased porosity evolution rates for all sizes, with the largest effects observed for medium (5.26) and large (13.72) pellets. The curvature effect is pronounced in larger pellets, where the lower surface area to volume ratio can lead to a greater accumulation of hydrogen on the pellet surface, which increases the reduction rate and porosity evolution. Smaller pellets, which have a greater curvature, tend to distribute stresses more evenly during