EFEITO DA BASICIDADE BINÁRIA E DO TEOR DE MgO NO INCHAMENTO DE PELOTAS DE MINÉRIO DE FERRO*

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Resumo
O inchamento é um grande problema durante a redução de pelotas de minério de ferro. Várias mudanças podem ser feitas nas pelotas para minimizá-lo. Conforme o sínter utilizado se torna cada vez mais básico, pelotas mais ácidas são desejadas. A adição de MgO, assim como a modificação da basicidade binárias das pelotas pela adição de CaO são soluções que têm sido apontadas. Dessa forma, este trabalho estudou os efeitos do MgO a da modificação da basicidade binária nas seguintes propriedades de pelotas: compressão a frio, porosidade e índice de inchamento. Foram preparadas pelotas com até 5% de MgO e com basicidades entre 0,67 e 1,5. O aumento do teor de MgO causou aumento de porosidade e queda de resistência. A basicidade diminuiu a porosidade e causou aumento de resistência nas pelotas de basicidade 1,0. Tanto o aumento de basicidade quanto a adição de MgO diminuíram o inchamento.
Palavras-chave: Inchamento; Minério; Pelotas

EFFECT OF BINARY BASICITY AND MgO CONTENT IN THE SWELLING OF IRON ORE PELLETS

Abstract
Swelling is a major problem during reduction of iron ore pellets. In order to decrease it, several modifications can be made in the pellets. As sinter gets each time more basic, lower basicity is desired for pellets. Addition of MgO as well as basicity modification by addition of lime has been pointed out as possible solutions. Based on this, this work studied the effects of MgO addition and basicity modification on the following properties of pellets: cold compression strength (CCS), porosity and swelling index. Pellets with additions up to 5% of MgO and basicity in a range of 0.67 to 1.5 were prepared. Porosity increased with MgO addition, and decreased with basicity; CCS decreased with MgO and increased with basicity up to 1.0, and then decreased. MgO additions and basicity increment helped to decrease swelling.
Keywords: Swelling; Ore; Pellets.

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1 INTRODUCTION

The swelling of iron ore pellets may occur during reduction in blast furnaces, generating problems such as breakage and formation of fines, which can cause disruption in gas flow [1]. The main causes for swelling are the phase transformation during reduction of hematite to magnetite and the growth of iron whiskers during the reduction of wüstite [2, 3]. Many attempts have been made to improve their performance by adding flux such as MgO and/or modifying the binary basicity (CaO/SiO_2). [4, 5, 6]

Frazer et al [4] studied the effect of basicity and of the amount of gangue on swelling behavior of pellets. They found a peak of swelling when basicity was in the range of 0.2 to 0.8. They attributed this increase to the formation of low melting point slag (olivine) during the reduction, which cannot hold the particles together and allows whiskers to grow freely.

Sharma et al [5] also performed tests with addition of CaO in iron ore pellets and they found that for pellets with firing temperature higher than 1000°C, CaO formed ferrites when in contact with iron oxides, and these ferrites could cause decrease in swelling.

Addition of MgO can decrease swelling in pellets. According to Dwarapudi et al [6], the presence of MgO in iron ore pellets can create a high melting point gangue, which acts as bond during reduction, decreasing mobility of the particles. It has also been reported [3] that Mg^{2+} in wüstite decreases swelling due to whisker formation, since it is a smaller ion than the Fe^{2+} ion (0.60 Å for Mg^{2+} and 0.74 Å for Fe^{2+}). According to Nicolle and Rist model for whisker formation, smaller ions inside the wüstite lattice decrease the diffusivity of Fe^{2+} ions, which hinders whisker formation.

This work aimed to verify the effect of addition of MgO and basicity modification in pellets for blast furnace regarding their physical properties, and swelling behavior.

2 EXPERIMENTAL PROCEDURE

Pellets of different compositions were produced in a disc pelletizer of 1.2 m of diameter under 17 rotations per minute. The composition of the iron ore blend is shown in Table 1. It is important to note that the used ore was already mixed with coal and some lime, which created a blend with basicity 0.76. During pelletizing 0.5% of bentonite (Table 2) was added to be used as binder, so the minimum binary basicity reached was 0.67.

Limestone (composition in Table 3) was added to provide three basicity levels: 0.67, 1 and 1.5. To each of these levels, 0%, 1% and 5% of P.A. MgO were added. Thus, a total of nine compositions were prepared. The pellets were indurated at 1300 °C for a period of 15 minutes in air atmosphere. The heating profile is shown in Figure 1. After the holding period at high temperature, pellets were immediately removed from the furnace and cooled in air.

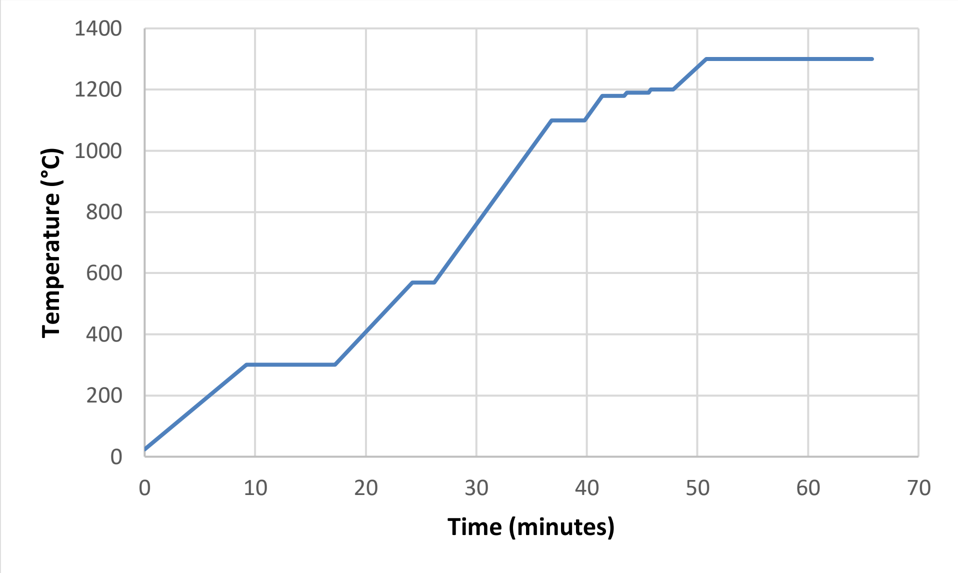

Figure 1. Heating profile of the furnace during firing of the pellets.

Table 1. Composition of the iron ore blend

Component	wt.%
SiO_2	1,18%
Al_2O_3	0,45%
Fe_2O_3	96,00%
MgO	0,04%
CaO	0,90%
TiO_2	0,06%
P	0,04%
Mn	0,09%
LOI	0,12%
C fixed	1,11%

**LOI: loss on ignition*

Table 2. Composition of the bentonite used during palletization

Component	wt.%
SiO_2	57,77%
Al_2O_3	16,19%
Fe_2O_3	4,40%
MgO	2,58%
CaO	0,66%
K_2O	0,94%
TiO_2	0,94%
LOI	10,71%

Table 3. Composition of the limestone used to adjust basicity.

Component	wt.%
SiO2	4,78%
Al2O3	0,52%
MgO	3,52%
CaO	49,25%
LOI	40,80%

Porosity of the fired pellets was measured using an image analyzer software. Six pellets were randomly selected from each batch. Ten images of each pellet were taken with a stereomicroscope. With these images, the software could calculate the total volume of the pellet. The mass of the pellet was also weighed for determining the apparent density. Finally, the software compared the apparent density with a data base of density of iron ore pellets based in the iron content.
Cold compression strength of the fired pellets was also measured in a press EMIC. The load cell used was for 10 kN and the speed of the test was 0.25 mm/min.
Reduction tests were based in ISO Standard 4968 for free swelling of pellets. They were carried out in a ceramic retort inside a furnace (Figure 2-a). A diagram of the experimental set up is shown in Figure 2-b. Six pellets were laid on an alumina bed. The gas was flowed upwards from the bottom of the retort through this bed until it reached the pellets. Temperature of the tests was 900 °C measured with the thermocouple touching the pellets. The reduction gas was composed of 4.5 NL/min of CO (30 vol%) and 10.5 NL/min of N_2 (70 vol%) and was kept flowing for a period of one hour.
Reduction degree was determined by the mass difference of pellets before and after reduction. This mass difference was considered as the oxygen removed by the reduction reaction. Finally, reduction degree was obtained by dividing the removed oxygen by the total amount of oxygen bounded to iron in the pellet.
Pellet volume was measured before and after the reduction using the same image analyzer used for porosity measurements. Swelling index was calculated according to Equation 1, where V_f is the final volume of the pellets and V_i is the initial volume:

$$\%\, swelling = \frac{V_f - V_i}{V_i} \times 100\% \tag{1}$$

Microscopic analysis of fired and reduced samples was conducted. Scanning Electron Microscope (SEM) with Energy Dispersive X-Ray Analysis (EDS) was used for such analysis.

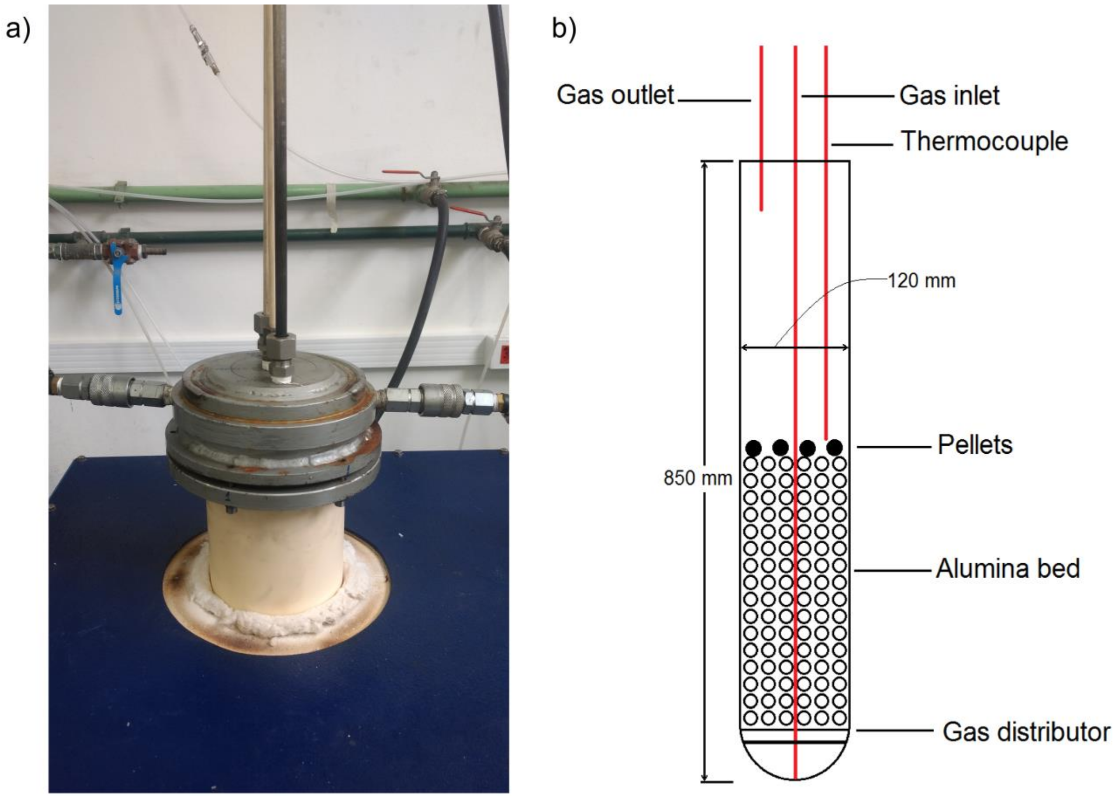

Figure 2. a) Experimental apparatus used to reduce the pellets. b) Sketch of the experimental apparatus.

3 RESULTS

Cold compression strength (ccs) of the fired pellets is shown in Figure 3. It can be seen that the compression strength of the pellets decreases as MgO level increases, regardless the basicity. Basicity increment up to 1.0 led to improvement in ccs of the pellets, but further increment to 1.5 decreased strength.

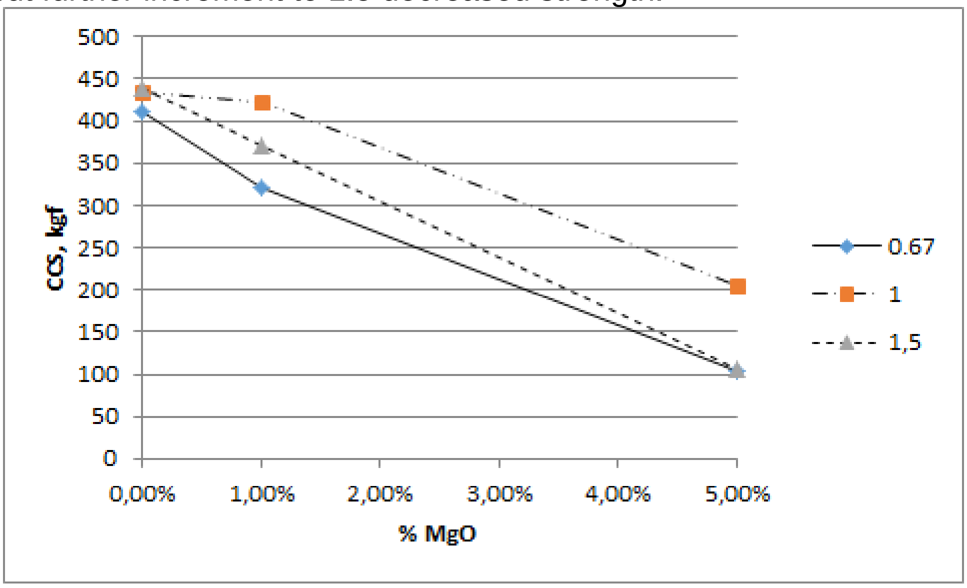

Figure 3. Cold compression strength for fired pellets.

The porosity of the fired pellets is shown in Table 4. Porosity did not show big changes for 1% addition of MgO, presenting values within experimental error, but showed a big increment for MgO 5%. In terms of basicity, acid pellets showed higher porosities. Nonetheless, this does not reflect the behavior observed for strength.

Table 4. Porosity of the fired pellets

Basicity	MgO (wt.%)		
	0	1	5
0.67	35,80%	35,03%	42,16%
1	35,57%	33,81%	38,69%
1.5	33,20%	33,48%	39,44%

Results for swelling tests are shown in Table 5 and reduction degree in Table 6.

Table 5. Swelling of pellets after 60 minutes reduction in 70/30 CO/N_2 gas flow

Basicity	MgO (wt.%)		
	0	1	5
0.67	22,43%	15,51%	7,86%
1	11,93%	11,42%	6,41%
1.5	17,09%	9,61%	15,65%

Table 6. Reduction degree after 60 minutes reduction in 70/30 CO/N_2 gas flow

Basicity	MgO (wt.%)		
	0	1	5
0.67	31,63%	45,21%	62,09%
1	53,67%	59,29%	70,56%
1.5	42,52%	56,04%	61,04%

At first, it seems clear that MgO addition and basicity increase does indeed decreases the swelling for basicity 0.67 and 1.0. Pellets with basicity 1.5 showed a different behavior than the others, showing an increment of swelling in high levels of MgO. But different degrees of reduction are achieved for the different pellets, and the reduction degree causes different swelling in pellets. Reduction degree agrees with porosity, that is, fired pellets with higher porosities yielded higher reduction degrees.
SEM images for some compositions of fired and reduced pellets are shown in Figure 4 along with EDS analysis of some phases in Tables 7, 8, 9 and 10.

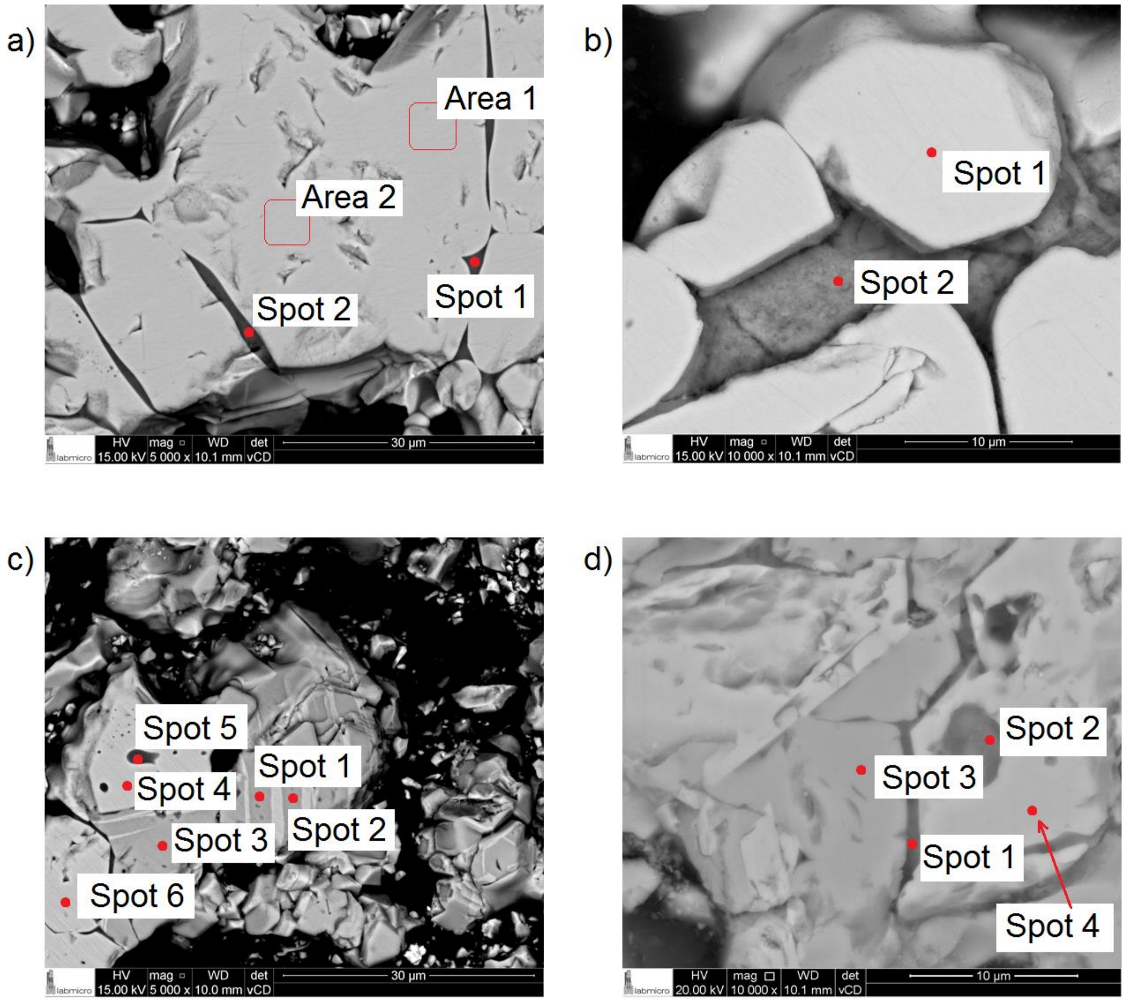

Figure 4. SEM images of pellets of the following compositions: a) basicity 0.67, MgO 0%; b) basicity 1.5, MgO 0%; c) basicity 0.67, MgO 5%; d) basicity 1.5, MgO 5%.

Table 7. EDS analysis of the pellet with composition: basicity 0.67, MgO 0%

Basicity 0.67; MgO 0%								
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	Fe_2O_3
Spot 1	0,32%	0,87%	2,99%	42,38%	3,14%	0,27%	34,18%	15,84%
Spot 2	0,07%	0,59%	2,84%	39,85%	2,30%	0,29%	32,81%	21,26%
Area 1	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	100,00%
Area 2	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	100,00%

Table 8. EDS analysis of the pellet with composition: basicity 1.5, MgO 0%

Basicity 1.5; MgO 0%								
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	Fe_2O_3
Spot 1	0,00%	0,00%	0,46%	0,00%	0,00%	0,00%	0,00%	99,54%
Spot 2	0,00%	0,00%	0,00%	14,97%	0,58%	0,00%	79,69%	4,76%

Table 9. EDS analysis of the pellet with composition: basicity 0.67, MgO 5%

Basicity 0.67; MgO 5%								
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	Fe_2O_3
Spot 1	0,00%	14,72%	1,21%	0,00%	0,00%	0,00%	0,00%	84,07%
Spot 2	0,00%	15,03%	0,98%	0,00%	0,00%	0,00%	0,00%	83,99%
Spot 3	0,00%	11,93%	0,78%	0,00%	0,00%	0,00%	0,00%	87,30%
Spot 4	0,00%	0,00%	0,57%	0,00%	0,00%	0,00%	0,00%	99,43%
Spot 5	0,19%	4,32%	3,31%	30,47%	1,92%	0,00%	23,75%	36,04%
Spot 6	0,00%	0,00%	0,40%	0,00%	0,00%	0,00%	0,00%	99,60%

Table 10. EDS analysis of the pellet with composition: basicity 1.5, MgO 5%

Basicity 1.5; MgO 5%								
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	Fe_2O_3
Spot 1	0,00%	4,56%	0,00%	16,50%	0,48%	0,00%	37,39%	41,06%
Spot 2	0,00%	0,00%	0,00%	0,32%	0,00%	0,00%	2,04%	97,63%
Spot 3	0,00%	18,59%	1,51%	0,00%	0,00%	0,00%	1,08%	78,82%
Spot 4	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%	100,00%

A phase with presence of Mg and Fe is formed in 5% MgO pellets (Figure 4-c and 4-d), and it is well distributed along the whole pellet. It can also be seem that smaller particles and bigger pores are present in these pellets compared to low MgO.

4 DISCUSSION

Phases with low melting point are created when little amounts of Ca^{2+} diffuses into Fe_2O_3 in air. These phases melt under 1250°C when the CaO content, in a mixture with Fe_2O_3, is below 40% [7]. This is expected to happen in the pellets during firing and the said liquid phase acts in the densification of the pellets. Moreover, higher gangue content leads to higher amounts of slag during firing, hence improving densification. Porosity values (Table 4) showed a decreasing tendency with increasing values of basicity, which agrees with the expected more intense densification.

Higher strength is usually correlated with higher densifications. The increase of the pellet strength from basicity 0.67 to 1.0 can be explained by this. However, a different tendency was observed when basicity was increased further to 1.5. The reasons for this tendency are yet not clear, however, one possibility is that phases with smaller strength are formed in high basicity pellets.

In Figure 4-d, spot 1, there is a thin continuous phase among hematite grains. This phase is likely to be the liquid or semi-liquid phase formed during firing. It shows a small amount of MgO just beside an area where Mg and Fe contents are high (spot 3). This is within the solid grains and could be a magnesioferrite ($MgO.Fe_2O_3$) formed as a result of the interaction of MgO and hematite. Further DRX tests are being conducted to verify this.

Addition of MgO leads to increase in porosity (Table 2). It has been reported [6] that MgO can lead to the formation of higher melting point phases, what could be a cause for higher porosity. Magnesioferrite ($MgO.Fe_2O_3$) can form when MgO reacts with Fe_2O_3. This phase is a spinel with high melting point, but it can be formed in lower temperatures, such as 1000 °C, by diffusion in solid state [5]. Hence, in firing temperatures used in this work it could be expected that it would form to some extent in iron ore pellets that contain MgO.

It has been reported [8] that magnesioferrite during reduction can slow the reaction rate due to the formation of magnesiowustite in later stages of reaction. However, it seems that the increment generated in the porosity of the pellets is enough to compensate this in some degree, because higher MgO pellets were able to reach higher degrees of reduction despite of the presence of magnesioferrite.

It is important to note, however, that simultaneous high amounts of MgO and CaO (binary basicity 1.5 and MgO 5%) can promote higher swelling. In this composition, major cracks appeared, as shown in Figure 6. Since the stereomicroscope only obtain a projection to calculate the volume, it does not take into account cracks, what may explain the larger swelling experienced in these pellets. After further examination of these pellets, it was noticed that even the fired ones had some inner cracks. During reduction, there is a natural embrittlement of iron ore pellets due to the destruction of hematite bridges between particles. Allied with the swelling and the preexisting cracks, this could be the cause for the bigger cracks and the bigger swelling measured for this composition.

Figure 6. Some of the reduced pellets for basicity 1.5 and MgO 5%, showing major cracks.

No whisker was observed in SEM images, even in low basicity and low MgO pellets, where they were expected. For most SEM images of reduced pellets, it seems that the reduction occurred on the surface of the particle, creating a layer of iron around it. This layer is what is expected when reduction occurs in a topochemical way. According to Nicole and Rist mechanism for whisker formation, this is related with reaction rates higher than diffusion rate of iron in the particle, which is a situation that does not allow growth of iron whiskers.

Besides that, high firing temperature can create a smoother surface in the pellets due to recrystallization of the iron oxide particles. This eliminates surface imperfections which are preferable sites for nucleation of iron. So, with smoother surfaces, nucleation can happen all along the particle, creating this layer of iron around it.

Without whiskers, swelling can be attributed to crystalline changes in the transformation from hematite to magnetite [2]. This stage of the reaction is accompanied by volume increase, that creates tension in the hematite matrix and, ultimately, cracks are generated. A crack within the hematite matrix is shown in Figure 7.

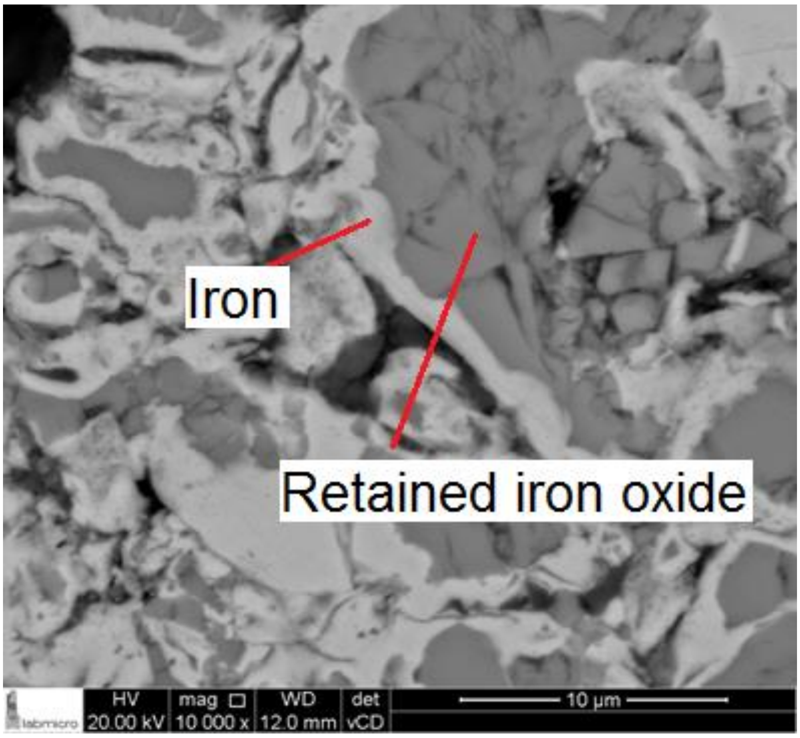

Figure 7. Crack within iron oxide matrix due to reduction stress.

Another effect not taken into account is the maximum swelling. According to the ISO Standard used as basis for the reduction tests, the swelling must be measured only after one hour of reduction. But due to different reaction rates, different reduction degrees are achieved in the test.

Reduction degree also plays a role in the swelling index. To check this, one reduction experiment was made with pellet of basicity of 1.5 and MgO of 1% for 20 minutes instead of 60 minutes. The results showed reduction degree of 42.62% and 14.46% swelling, against 57.45% reduction and 9.61% swelling in the pellet reduced for one hour.

Therefore, the pellet suffered swelling first and then some shrinkage. This could also happen to the other compositions. Therefore, this effect should be further investigated controlling reduction degree instead of time and measuring swelling for various reductions degrees.

5 CONCLUSION

Addition of CaO in the form of limestone to change the binary basicity (CaO/SiO_2) of iron ore pellets causes lower porosity. Higher strength values were found for basicity 1.0. MgO can cause higher porosities in pellets, which is good for reducibility, but in higher levels it causes decreasing in strength.

None of the swelling tests showed whisker formation. Higher basicity and MgO content can cause decrease in the swelling index of pellets, except when both, basicity and MgO, values are high

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