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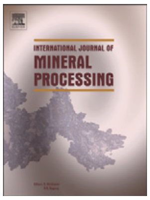

Disintegration on heating of a Brazilian manganese lump ore

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ABSTRACT

This pioneering study characterized the chemical, physical and mineralogical aspects of the Urucum Standard manganese ore typology, and evaluated some of its metallurgical characteristics, such as the main mineral heat decompositions, and the particle disintegration at room temperature and under continuous heating. A one-ton sample of ore was received, homogenized and quartered. Representative samples were collected and characterized with the aid of techniques, such as ICP-AES, XRD, SEM-EDS, BET and OM. Representative samples with particle sizes between 9.5 mm and 15.9 mm were separated to perform tumbling tests at room temperature, and thermogravimetry tests for both air and nitrogen constant flow at different temperatures. After each heating cycle, the mechanical strength of the ore was evaluated by means of screening and tumbling procedures. The Urucum Standard typology was classified as an oxidized anhydrous ore, with a high manganese content (~47%). This typology is mainly composed of cryptomelane and pyrolusite; however there is a significant amount of hematite. The Urucum Standard particles presented low susceptibility to disintegration at room temperature, but as temperature increased, susceptibility increased. No significant differences were observed between the tests done with the air or nitrogen injections.

1. Introduction

In the reducing process, the manganese lump ores have been widely applied as the main raw material for manganese ferroalloy production in electric furnaces (Olsen et al., 2007; Faria et al., 2010, 2012).

Pre-reduction is the critical zone of the electric furnaces, where the solid raw-materials are heated while descending into the furnace. The charge temperature is between 500 °C and 1100 °C (Tangstad and Olsen, 1995; Olsen et al., 2007; Faria et al., 2009). The moisture water is evaporated and the manganese oxides start their reduction due to the ascendant CO flow. Aiming for process efficiency, the charge permeability should be high and homogeneous inside the furnace (Olsen et al., 2007). According to Tangstad and Olsen (1995), if a big amount of fines were generated or placed in the pre-reduction zone, the charge permeability can widely decrease and the hot gases will be redirected, building some preferential paths within the solid matter. Under these conditions the charge will not be homogenously heated; a part of its moisture will not be removed and a big amount of oxides will not be completely pre-reduced. The output gases will be at high temperature and rich in CO, indicating an increase in energy consumption per ton of produced alloy (Olsen et al., 2007).

In this context, unexplored important metallurgical properties such as the cold and heat disintegrations of the manganese lump ores are presented herein. International standards for iron lump ores set the parameters used to characterize this property. However, for manganese lump ores disintegration, there are no existing characterization standards. Only three articles were found about the theme in scientific literature (Faria et al., 2010; Reis et al., 2010; Yoshikoshi et al., 1983).

Faria et al. (2010) studied the decrepitation behavior of three different Brazilian manganese ore typologies. Faria et al. used 15 kg of each ore, with particle sizes between 19 mm and 6.3 mm, and submitted the samples to heat shock in a pre-heated oven at 700 °C. After natural cooling the sample, the amount of particles below the 6.3 mm, 3.35 mm and 1.18 mm sieves were measured, and showed that the studied typologies presented different behaviors, as a function of their mineralogy and physical properties. According to Faria et al., the ore moisture generally increases fine generation. In 2012, Faria et al., using a similar methodology, made a complementary study about the ore decrepitation behavior. They studied three Brazilian ores and one South African, and correlated their decrepitation to their mineralogical and physical characteristics.

Tangstad et al. (2004) studied the mechanical resistance of three different manganese ores under a reducing atmosphere. Ore samples with particle sizes between 10 mm and 15 mm were heated up to 1100 °C in an atmosphere of 70%CO and 30%CO_2. The samples were tumbled, and

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Table 1
Global sample and studied size range chemical analysis.

Amostra	Mn %	Fe %	SiO_2 %	P %	Al_2O_3 %	CaO %	MgO %	TiO_2 %	BaO %
Global Sample	46.49	12.00	1.08	0.26	1.390	0.199	0.115	0.139	0.243
<15.9 e >9.5 mm	48.00	10.70	0.67	0.29	1.410	0.200	0.140	0.120	0.330

the amounts of generated fines were measured. According to Tangstad et al. (2004), the greatest amount of fines was obtained for the most porous ores, which corresponds to the richest in moisture.

Yoshikoshi et al. (1983) described some manganese ore properties. The particle sizes used in this study were between 14.9 mm and 12.7 mm. The methodology consisted in the heating of 500 g of ore up to 1000 °C in a muffle furnace with controlled inert atmosphere, made by a continuous flow of 100%N_2. At 1000 °C the muffle was turned off and the sample was cooled naturally to room temperature. The particle disintegration was measured by the fine weight below the 5 mm sieve, after 900 rotations in a bench scale tumbler. According to Yoshikoshi et al. (1983), the studied ore disintegration index was 63%.

Nowadays, the nomenclature and indexes which differentiate the steps of this disintegration are being discussed and there is still no consensus. As such, the aim herein is to help understand the decrepitation phenomena in manganese ores by characterizing the chemistry, the physics and the mineralogy of the Urucum Standard typology. To do this particle size disintegration at room temperature or under heat in an oxidizing or inert atmosphere was evaluated.

2. Materials and methods

2.1. Chemical, physical and mineralogical characterization

One ton of Urucum Standard ore was homogenized and quartered to produce a 50 kg sample. The reference sample (global) had particle sizes between 6.3 mm and 50 mm. Another sample with the same range was screened for particle sizes between 9.5 mm and 15.9 mm, which were characterized and destined for disintegration studies.

The characterization procedures consisted of determining the Mn, Fe, CaO, MgO, SiO_2, Al_2O_3, TiO_2 and P contents. The method used for this analysis was the atomic emission spectrometry from a plasma source (ICP-AES). Main minerals were identified by X-ray diffraction, in a Rigaku, model Geigerflex diffratometer with a copper tube. The scanning applied rate was 1.2°/min.

The apparent and structural densities were respectively determined by a water picnometer and by a Quantachrome helium multipicnometer. The specific surface area and the porosity were also determined by a Quantachrome BET device.

2.2. Particle disintegration

Aiming to evaluate ore particle disintegration, this work proposes to create a new terminology to describe and quantify the mechanical behavior of manganese lump ores. Two indexes are proposed: the CDI (*Cold Disintegration Index*) and the HDI (*Heat Disintegration Index*).

The CDI index allows evaluating the mechanical behavior of ores at room temperature, measuring their resistances to impact and abrasion. CDI was proposed mainly as a reference number for comparisons with the measurements at high temperature (HDI). The latter index allows evaluating the ore fine generation under continuous heating in the electric furnace pre-reduction zone.

Table 2
Mineralogy of the studied size range.

Sample	Minerals (%)			
	Cryptomelane (KMn_8O_{16}) Pyrolusite (MnO_2)	Hematite (Fe_2O_3)	Quartz (SiO_2)	Others
Urucum Standard <**15.9 e** >**9.5** mm	<80 e >70	<20 e >10	<10 e >5,0	<4

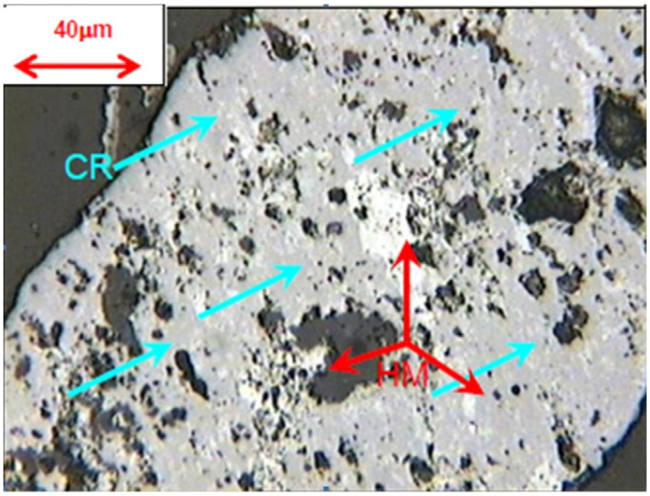

Fig. 1. Micrograph of an Urucum Standard particle (reflected light optical microscope). CR – Cryptomelane, HM – Hematite.

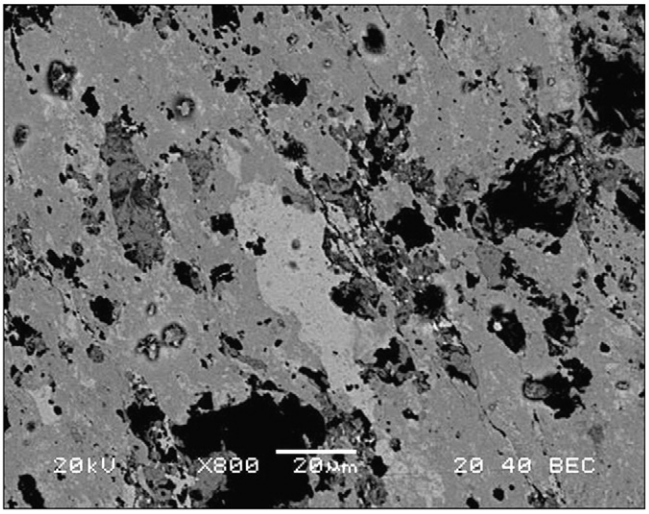

Fig. 2. Back scattered electrons image of an Urucum Standard particle.

Table 3
Structural and apparent densities.

Samples	Urucum Standard (Global)	Urucum Standard (<15.9 e >9.5 mm)
Apparent Density (g/cm^3)	3.9	3.8
Structural Density (g/cm^3)	4.3	4.0
Total Porosity (%)	9.1	4.0

Table 4
Porosimetry data obtained by nitrogen adsorption (BET).

Sample	Specific surface (m^2/g)	Total volume of pores 0.3–500 nm (cm^3/kg)	Average diameter of pores (Å)	Volume of micropores 0.3–2 nm (cm^3/kg)	Micropores Area 0.3–2 nm (m^2/g)	Maximum Size of Pores (Å)
Urucum Standard Global	11.52	35.21	122.3	5.4	15.34	1295.4
Urucum Standard <15.9 e >9.5 mm	9.05	30.62	135.3	4.2	11.98	1338.3

The ore particles from 9.5 mm to 15.9 mm were selected for the experimental procedures. The samples were homogenized and quartered until small representative samples with 2 kg were obtained. These samples were dried at 105 ± 5 °C and screened again in a 9.5 mm sieve. Then, the weight of material retained in 9.5 mm was quartered into 500 g samples. These samples were submitted to the CDI and HDI measurements.

Aiming to determine the CDI indexes, three samples of 500g were tumbled, at room temperature, during 10, 20 and 30 minutes in a rotating tumbler AN4696TR (ISO standards) with a diameter of 130 ± 2 mm and a length of 200 ± 2 mm. The utilized rotating frequency was 30 ± 1 rpm. For each tumbling time, the samples were classified using the following sieves: 9.5 mm, 6.3 mm, 3.35 mm, 1.18 mm, 0.6 mm and 0.15 mm (100#). The CDI indexes were calculated by the average weight of material produced below each size.

Aiming to determine the HDI indexes, the samples of 500 g were submitted to continuous heating (10 °C/min), going from room temperature until a pre-determined temperature, where the ore particles remained for an hour. The equipment utilized was an ISO standardized furnace equipped with a thermobalance. Three pre-determined tested temperatures were: 500 °C, 700 °C and 1000 °C. Two testing atmospheres were tested: static air and 100% of N_2 (5Nl/min).

The samples were cooled naturally at room temperature. After sample cooling, the particles were submitted to a particle size classification in a sieve of 6.3 mm, for the determination of the HDI index without tumbling. After that, the samples were tumbled, at room temperature, during 10, 20 and 30 minutes in a rotating tumbler AN4696TR. For each tumbling time, the samples were classified using the following sieves: 9.5 mm, 6.3 mm, 3.35 mm, 1.18 mm, 0.6 mm and 0.15 mm (100#). The HDI indexes were calculated by the average weight of material found below each mesh size. In this article, as the critical particle size for the ferroalloy production is 6.3 mm, only the indexes measured in this sieve are presented.

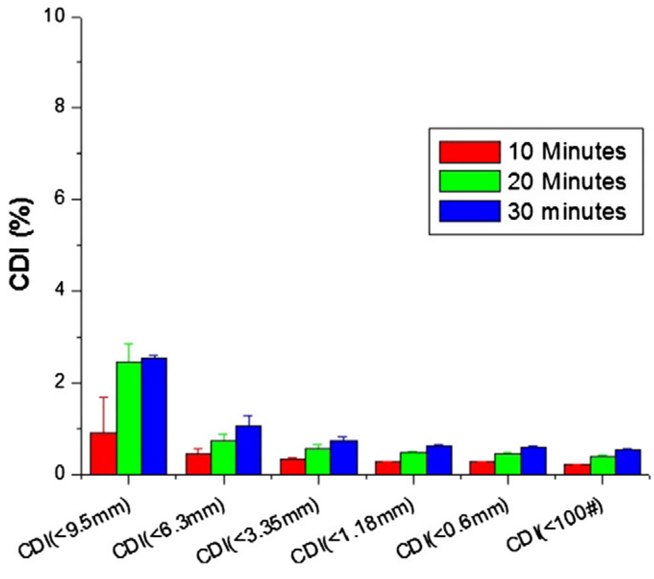

Fig. 3. Cold disintegration indexes (CDI).

3. Results and discussions

3.1. Chemical, physical and mineralogical characterization

Table 1 shows the sample dry-basis chemical analysis. Urucum Standard ore is rich in Mn, where ore particle sizes from 9.5 mm to 15.9 mm form the richest fraction, but with a low Mn/Fe rate, around 4.8. The studied ore has a low SiO_2 content, with a low average binary basicity (CaO/SiO_2) of around 0.2. These values for the Mn/Fe rate and the binary basicity indicate that the ferroalloy manufacturer can produce a high metal/slag rate, but using more expensive ferriferous loads for the iron content adjustment in the furnace charge. The ore P content was high and is a problem for the ferroalloy plant.

The chemical characteristics are explained by the ore mineralogy. Table 2 presents the sample mineralogical constituents, and it was possible to observe that the Urucum Standard ore is typically oxidized, with cryptomelane predominance and an expressive hematite presence. This predominance justifies the high Mn and Fe contents. Fig. 1 presents a micrograph of an ore particle, obtained with reflected light optical microscope. It shows a cryptomelane matrix, which is dark gray in color, and a hematite crystal, which is white with high reflection power.

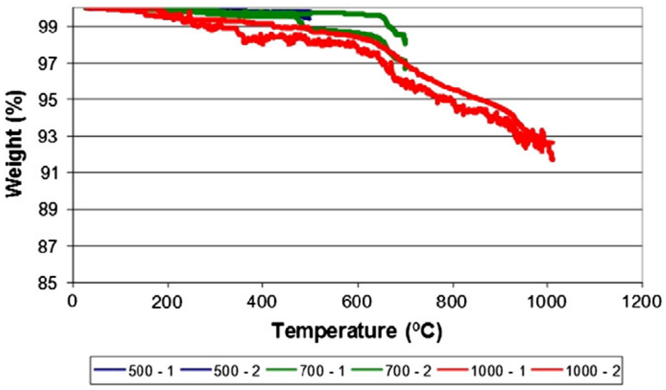

Fig. 4. Weight losses during heating in inert atmosphere (5Nl/min of 100% N_2).

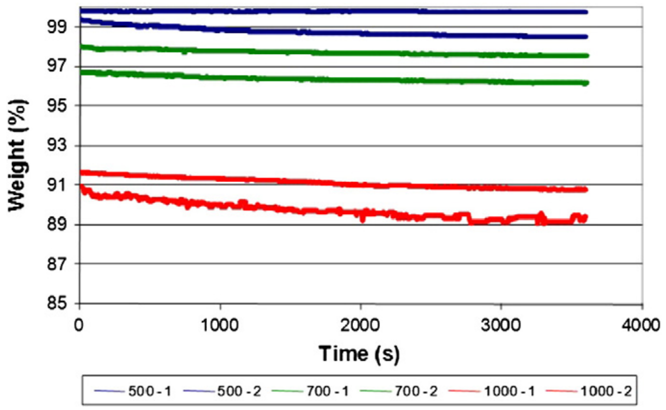

Fig. 5. Weight losses during isothermal heat treatments in inert atmosphere (10Nl/min of 100% N_2).

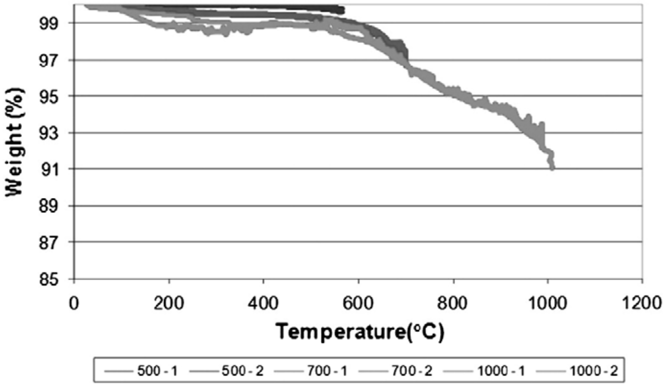

Fig. 6. Weight losses during heating in air atmosphere.

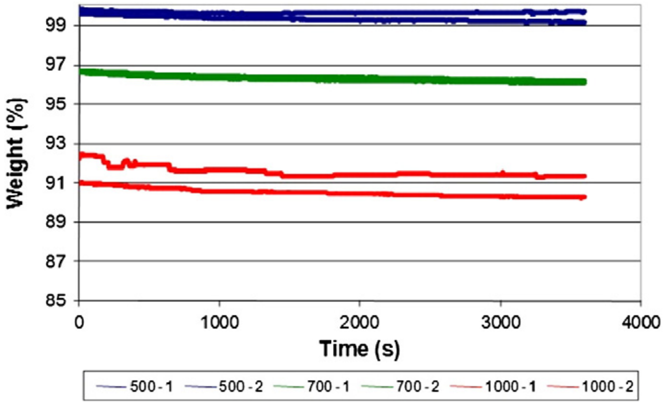

Fig. 7. Weight losses during isothermal heat treatments in air atmosphere.

Fig. 2 presents a back-scattered electron image of the same particle. The cryptomelane matrix and the hematite crystal are visible.

The structural and apparent densities were determined respectively by helium and water picnometry. Table 3 presents these results. The structural density (~4.2) was high and this value was justified by the high cryptomelane content, which is a high dense manganese oxide. It was noticed that the global sample was more porous than the range between 9.5 mm and 15.9 mm.

Table 4 presents the porosimetry data obtained by the nitrogen adsorption technique (BET). It is possible to affirm again that the global sample is more porous than the studied size range; consequently, it has a higher specific surface. However an important characteristic is that the size range between 9.5 mm and 15.9 mm has the largest pore average diameter.

Porosimetry data is an important parameter for ferroalloy production. Faria et al. (2012) showed that for manganese ores, a relationship between the total volume of pores and the decrepitation intensity exists. According to them, the higher the volume of pores, the more intense will be the decrepitation. Faria et al. (2012) also showed that the higher the average diameter of pores, the lower the decrepitation. Faria (2011) presented in his PhD thesis that the higher the relation between the volume of pores and the specific surface, the better the ore pre-reduction step in the electric furnace granular zone. It is possible to hope that the Urucum Standard ore presents considerable decrepitation behavior, mainly when it is wet. Due to its high porosity, it has a great facility to absorb moisture, and when fast heated, may crack catastrophically due to high pressure water vapor elimination.

3.2. Particle size disintegration

3.2.1. Cold disintegration index (CDI)

The cold ore disintegration indexes (CDI) and their standard deviations are presented in Fig. 3. The Urucum Standard typology has low susceptibility for fine generation at room temperature (~1% below 6.3 mm mesh after 30 min into the tumbler).

3.2.2. Heat decompositions and heat disintegration indexes (HDI)

Fig. 4 presents weight losses as a function of the heating temperatures in an inert atmosphere (5Nl/min of 100% N_2). Fig. 5 shows sample weight behavior during the isothermal heat treatments (500 °C, 700 °C and 1000 °C with 10Nl/min of 100% N_2). Fig. 6 presents weight losses during heating in a natural air atmosphere. Fig. 7 shows the weight as a function of the isothermal heat treatment times (500 °C,

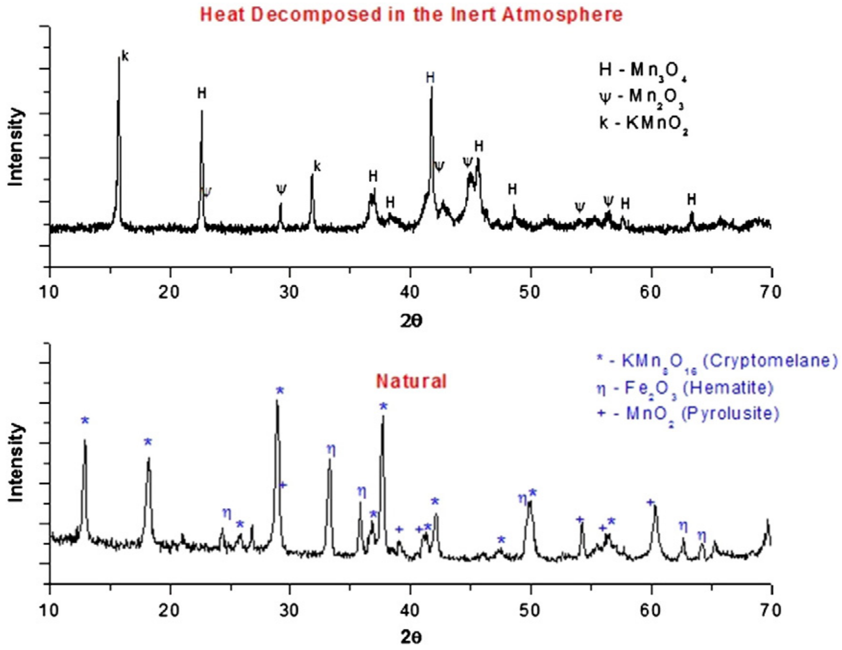

Fig. 8. Comparison between the heat decomposed (1000 °C in the inert atmosphere) and natural sample X-ray spectrums.

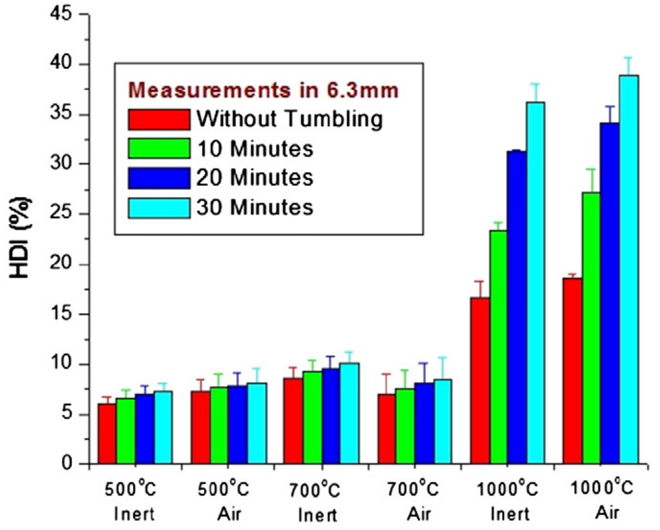

Fig. 9. Comparison between the heat disintegration indexes (HDI) measured in 6.3 mm mesh.

700 °C and 1000 °C under air continuous flow). Each condition was tested in duplicate.

There were no significant differences between the samples heated in the air and inert atmosphere. The small variations could be associated to the small mineralogical variability from one sample to the other. During the sample heating until 500 °C, an average weight loss of 0.4% was observed, related to the structural water elimination during the goethite heat decomposition, which starts at around 350 °C. Until 700 °C, an average weight loss of 2.5% was associated with the cryptomelane (KMn_8O_{16}) and pyrolusite (MnO_2) heat decompositions to Mn_2O_3. Only during the isothermal heat treatment, did all the oxides with +4 Mn valences seem to be decomposed into oxides with valence +3.

The oxides with Mn valences +3 (Mn_2O_3) start heat decomposition to Mn_3O_4 in temperatures of around 950 °C. Figs. 2 and 4 demonstrate the significant change in the weight loss rate around this temperature. The average weight loss after the 1000 °C isothermal heat treatment was 9%.

Fig. 8 presents X-ray diffraction spectrums for the natural and heat treated (1000 °C in the inert atmosphere) ore samples. It was possible to observe that after heating, the major phase was Mn_3O_4, but also a small amount of Mn_2O_3 existed.

Fig. 9 compares heated ore disintegration indexes (HDI) measured in the 6.3 mm sieve for the samples heat treated at 500 °C, 700 °C and 1000 °C in both the studied atmospheres. For 500 °C and 700 °C, the tumbling effect was very small. Considering the standard deviations, it was possible to affirm that the determined indexes at these temperatures were very close to each other. Previously discussed heat decomposition studies permitted to affirm that, for these temperatures, the most probable cause of the fine generation was structural water elimination. The water vapor increases the particle internal pressure and explodes catastrophically. The cryptomelane and pyrolusite decompositions to Mn_2O_3 have a small contribution at this stage.

The worst behavior was found for the heat decomposed samples at 1000 °C. $HDI_{-6,3\ mm}$ was the highest and the tumbling effect, more significant. This may be associated to the catastrophic rupture of particles, added to the crack growth and propagation during the tumbling. The catastrophic rupture, as already cited, may be caused by the water vapor pressure, and the cause of the cracking may be associated to the progress of cryptomelane and pyrolusite heat decompositions, which during their decomposition to Mn_2O_3, change their crystal volume.

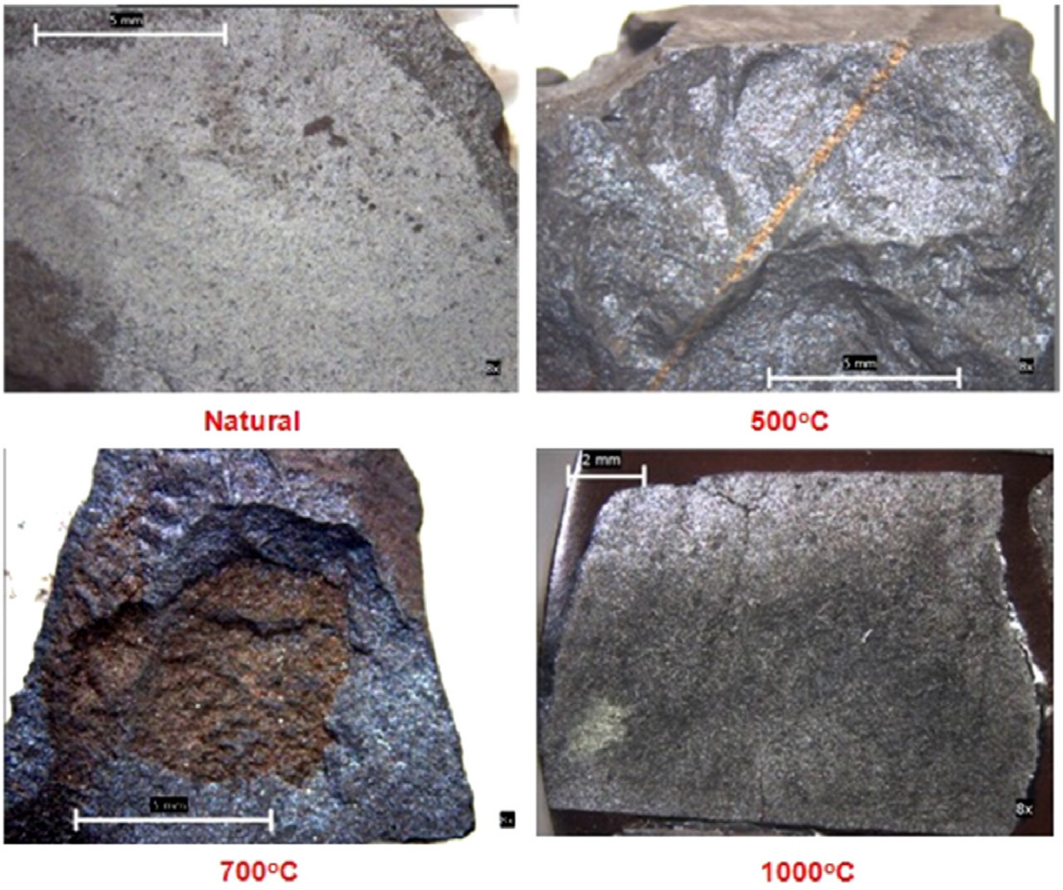

Fig. 10. Micrographs of Urucum Standard particles (Natural and heat decomposed in the inert atmosphere).

Mn_2O_3 decomposition to Mn_3O_4 may also contribute to this phenomenon. According to Faria (2011), the cryptomelane and pyrolusite have their volumes respectively 5.4% and 0.6% higher than the Mn_2O_3 volume, which is 0.7% smaller than the Mn_3O_4 volume.

Fig. 10 presents a comparison between the micrographs obtained with a reflected light stereomicroscope for natural and heat decomposed particles at 500 °C, 700 °C and 1000 °C in the inert atmosphere (100% of N_2). The natural surface was homogeneous, compact, but with notable porosity. The heated particles, decomposed at 500 °C and 700 °C, presented irregular surfaces with cavities that indicates abrupt material pullout. It was noticed that within these cavities, a high concentration of small orange crystals were present that could be associated with decomposed hydrated phases. The heated particles, decomposed at 1000 °C, presented their flatter and darker fractured surface, which indicated porosity increase and a change in the disintegration mechanism, now mainly governed by the decomposition of the oxides and anisotropic volume changes. After the isothermal treatment, but before the tumbling, different kinds of flat cracks were observed over the surface of the particles.

4. Conclusions

1. According to its mineralogical constituents and chemical composition, the Urucum Standard typology was classified as oxidized anhydrous. Due to its high manganese and low silica content, it is a good alternative for the ore mixtures confection in manganese ferroalloy plants. However Urucum Standard is not good enough to be the only Mn and Fe supplier in the production process due its high Mn/Fe (3.9) rate and P (0.26%) content.
2. The Urucum Standard typology presents low susceptibility to particle disintegration at room temperature. The CDI obtained, after 30 minutes of tumbling, were 1% below 6.3 mm and 0.6% below 1.18 mm.
3. There were no significant differences between the samples heated in the air and those in the inert atmosphere. The small variations could be associated with the small mineralogical variability of the samples. During the sample heating until 500 °C, structural water elimination occurred. Until 700 °C the cryptomelane (KMn_8O_{16}) and pyrolusite (MnO_2) decomposed to Mn_2O_3. The oxides with Mn valences +3 (Mn_2O_3) started its heat decomposition to Mn_3O_4 in temperatures at around 950 °C.
4. There were no significant differences between HDI measured in an inert atmosphere (100% of N_2) and in an oxidant atmosphere (natural air). The differences between the indexes measured for samples heat treated at 500 °C and 700 °C were very small. They are associated to the beginning of the cryptomelane and pyrolusite heat decompositions to Mn_2O_3 at around 600 °C. The indexes obtained for the samples heat treated at 1000 °C were the highest. This observation may be associated mainly to complete decomposition of cryptomelane and pyrolusite, as well as the Mn_2O_3 decomposition to Mn_3O_4.
5. The main causes for the heating particle disintegration of Urucum Standard ore were structural water elimination and crystal volume changes due to the heat decomposition of oxides.
6. For the studied manganese ore, it is possible to suggest that the decrepitation term should only be used to describe the fine generation during its fast heating rate up to temperatures of around 700 °C, where the structural water elimination is the main mechanism responsible for the catastrophic cracking of the particles, and the tumbling procedure has no great influence. For temperatures above 800 °C, the oxides heat decompositions significantly increase fine generation, due to crystal volume changes, induced internal tensions and crack growths. Under this condition, the tumbling procedure has a great influence in fine generation and the suggested reference term for this behavior may be Heated Ore Disintegration or Ore Pre-reduction Disintegration.

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