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EFFECTS OF REDUCTION PARAMETERS ON THE AMOUNT OF Pb, Zn, Cu and Cd IN REDUCED PELLETS. A CASE STUDY OF NIZNA SLANA IRON ORE PELLETS.

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ABSTRACT

A study of reduction of Nizna Slana Iron ore pellets using Hydrogen has been conducted. The structural and phase changes that occur in iron ore pellets at various temperatures have been investigated by scanning electron microscopy. The pellets were made from concentrates of Nizna Slana iron ore obtained from Slovakia, and were reduced at various temperatures in the range 600°C to 1200°C. It was found that recrystallization of hematite and melting of the gangue minerals present started at about 1100°C. At about 1150°C, the amount of Pb, Zn, Cd and Cu in the pellets were significantly reduced. Compressive strength measurements also showed that the strength of pellets reduced at 900°C or less were low compared to those of pellets reduced at 1150°C. At 1150°C, the observed fracture mode was transcrystalline.

KEYWORDS: Pellets, Temperature, Recrystallization.

INTRODUCTION

In recent times, there has been a phenomenal growth in the rate of production of Iron ore pellets. This is not altogether unexpected in view of the multifarious advantages that pellets offer to the blast furnace operator. Greater porosity, high crushing strength and faster reduction rates due to more accessible surface area per unit weight, lower divalent iron content and a low angle of repose besides the uniform size and shape are just a few attributes of pellets that have made such high production rates possible in modern blast furnace (Okeke, 1995, Singhal and Kanetkar, 1973).

The production of pellets of the right quality depends on the production of green balls having good physico-chemical properties, since the subsequent drying and firing cannot make good fired balls from poor quality green balls. The mechanical properties of pellets also depend on the chosen firing temperature and the resident time at the firing temperature, as well as on the rates of heating and cooling, (Majercak, 1977). The reduction of Iron ore pellets has been extensively studied, (Majercak, 1972; Ball, 1973). Various physical, chemical and polymorphic changes take place in pellets during preheating and firing.

All Iron ores contain impurities, which are collectively known as gangue. The impurities may be divided into slag forming and metallic oxides which are largely reduced to metal during iron making and deleterious impurities. Silica (SiO_2), alumina (Al_2O_3), lime (CaO) and magnesia (MgO) are slag forming impurities. Manganese, chromium, nickel, lead, zinc, Copper and cadmium oxides are metal oxides which are largely reduced to metal during iron making.

A Manganese content of about 1 per cent in the ore is advantageous but small proportions of other metals, e.g. Zinc, lead, chromium etc. in the ore are undesirable. Both sulphur and phosphorus are deleterious impurities and impart undesirable properties to steel and so must be kept below certain maximum levels. The removal of small portions of zinc, lead, copper and cadmium in reduced pellets has not been reported so far. It is therefore expedient to assess the behaviour of these metals during reduction of pellets.

In this paper, the balling of iron ores was carried out in a drum. The reduction experiments with Hydrogen have been used to reveal the reduction behaviour and reduction mechanism.

EXPERIMENTAL PROCEDURE

Preparation of Material

The Iron ore concentrate used in this work was obtained from Nizna Slana Pellet Plant. The composition of the concentrate is given in Table 1. The concentrate was mixed with 1.0%

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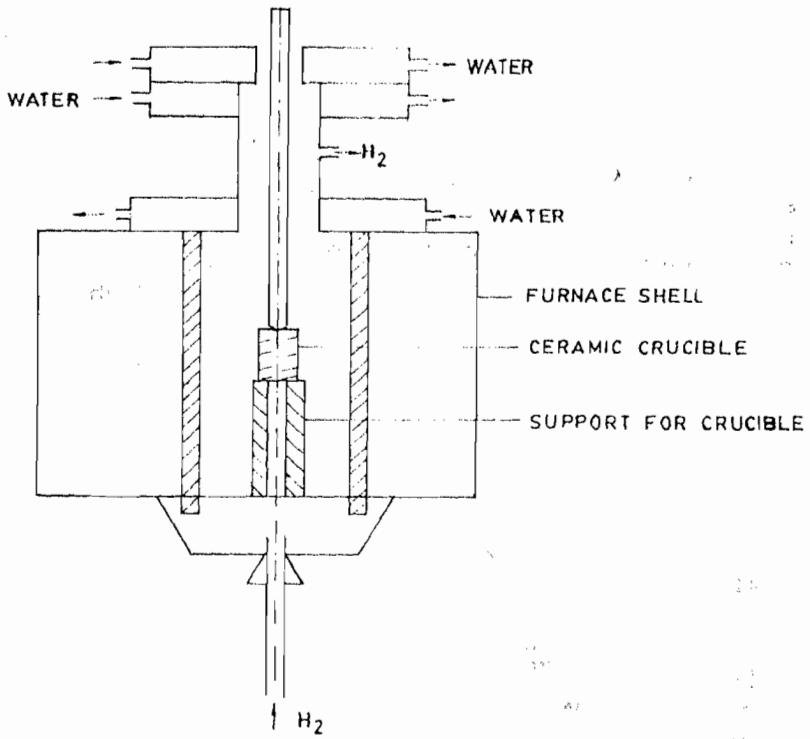


Fig. 1: DETAIL OF REDUCTION TECHNIQUE

bentonite to provide bonding and was then balled in a balling drum with an optimum moisture content of 11.8 wt per cent. Details of the procedure used are as described in (Ball, 1973). The green balls obtained were, on average, about 14mm in diameter.

Reduction Tests

Reduction tests were performed with hydrogen at a flow rate of 50 cm^3/min. The green balls were placed in a ceramic crucible and reduced in a reduction furnace (see figure 1) for one hour at various temperatures, namely, 600°C, 700°C , 800° C, 900°C, 1000°C and 1150°C. The green balls were heated to 600°C under nitrogen, then the hydrogen gas was passed up through the samples at the required flow rate. The change in mass and the temperature were continuously recorded by a personal computer. Pellets reduced at the various temperatures were subsequently subjected to fractographic analysis, the fracture surfaces being studied by scanning electron microscopy, using electron microscope SEM type ISM-35. The SEM was also used to study the concentration or composition of various elements at selected points on the fracture surfaces. Pellet samples reduced at 600°C, 800°C, 900°C, 1000°C, 1150°C and 1200°C were later subjected to mechanical tests to determine their compressive strengths.

RESULTS

Influence of Reduction Temperature on the amount of Zn, Pb, Cu and Cd in reduced pellets.

Figure 2 exhibits the influence of Reduction temperature on the amount of Zn, Pb, Cu and Cd in reduced pellets. At higher temperatures, there is significant drop in the amount of Zn, Pb, Cu and Cd in the reduced pellets. The largest drop was at the temperature of 1150°C. Zn, Pb and Cd dropped by About 65%. However, Cu did not show any significant drop up to the temperature of 1000°C.

Influence of Reduction time on the amount of Zn, Pb, Cu and Cd in reduced pellets.

Figure 3 illustrates the variation of the Zn, Pb, Cu and Cd in reduced Pellets as a function of reduction time at a constant temperature of 1150°C. The chemical analysis curves show that there is a marked drop in Zn, Pb, Cu and Cd content in reduced pellets at higher reduction times. After 60 minutes, there was no further weight loss for Zn, Pb, Cu and Cd in the pellets.

Influence of the diameter of pellets on the amount of Zn, Pb, Cu, and Cd in reduced

TABLE I: CHEMICAL COMPOSITION OF ORE CONCENTRATE

Constituent	FeO	Fe_2O_3	$(\sum Fe)^o$	SiO_2	CaO	MgO	Al_2O_3	Mn	P_2O_5	S	Zn	Cd	Pb	Cu
Composition %	2.11	71.87	(52.9)	7.27	3.47	8.77	1.47	3.3	0.14	0.14	0.007	0.015	0.006	0.021

TABLE II: COMPRESSIVE STRENGTH OF PRE-REDUCED PELLETS AT VARIOUS TEMPERATURES (Reduction time 60 min)

Temperature (°C)	600	800	900	1000	1150	1200°C
Compressive Strength (N/Pellet)	240	260	390	850	970	890

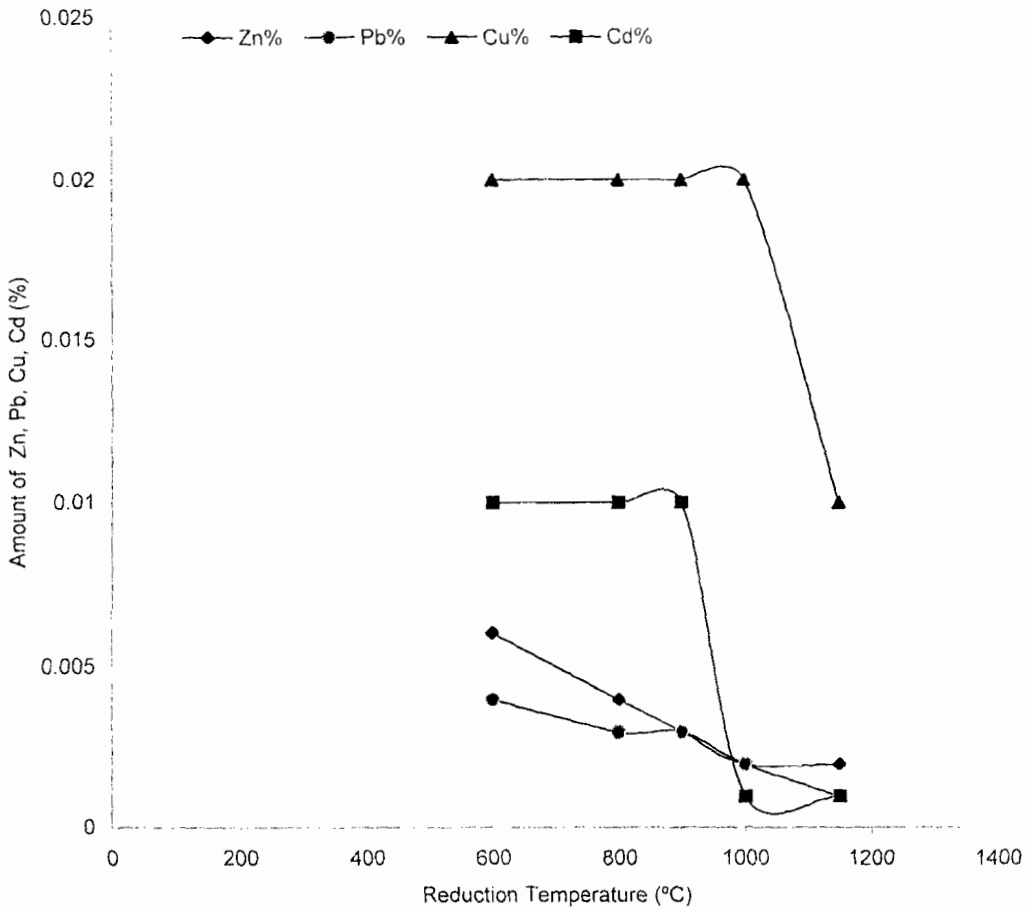


Figure 2: The amount of Zn, Pb, Cu and Cd in reduced pellets versus Temperature (Reduction time 60 min)

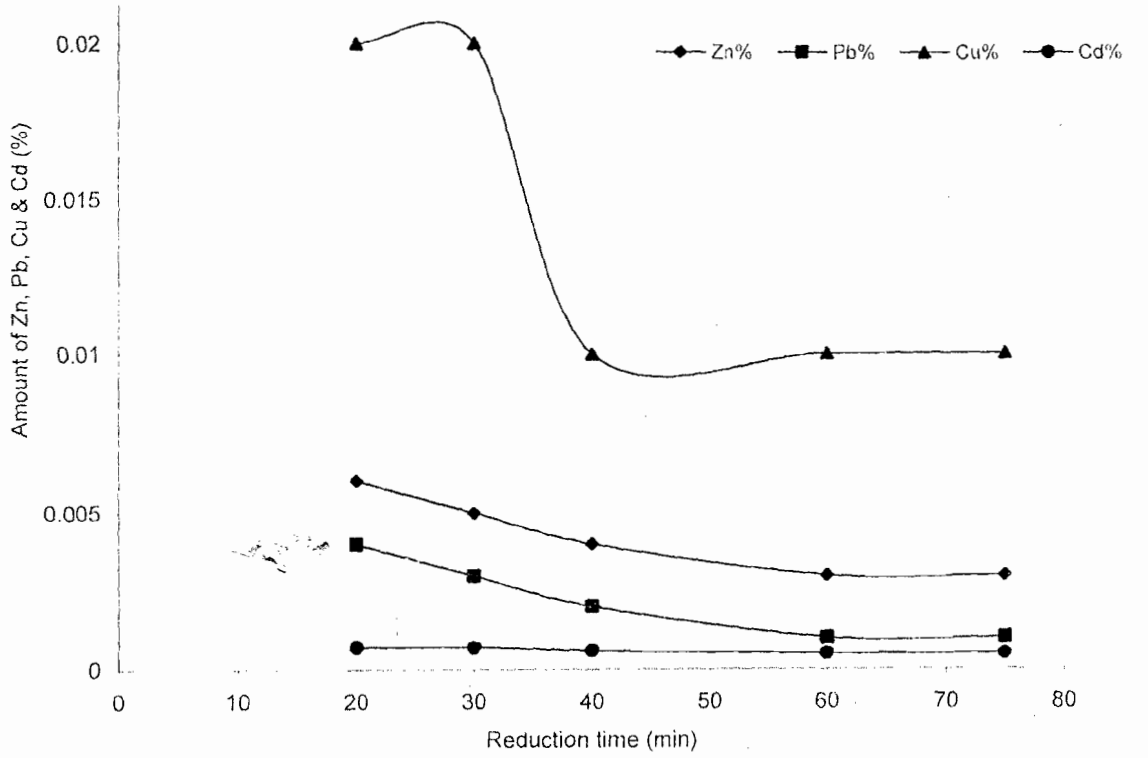


Figure 3: The amount of Zn, Pb, Cu and Cd in reduced pellets versus reduction time (Reduction Temperature 1150 °C)

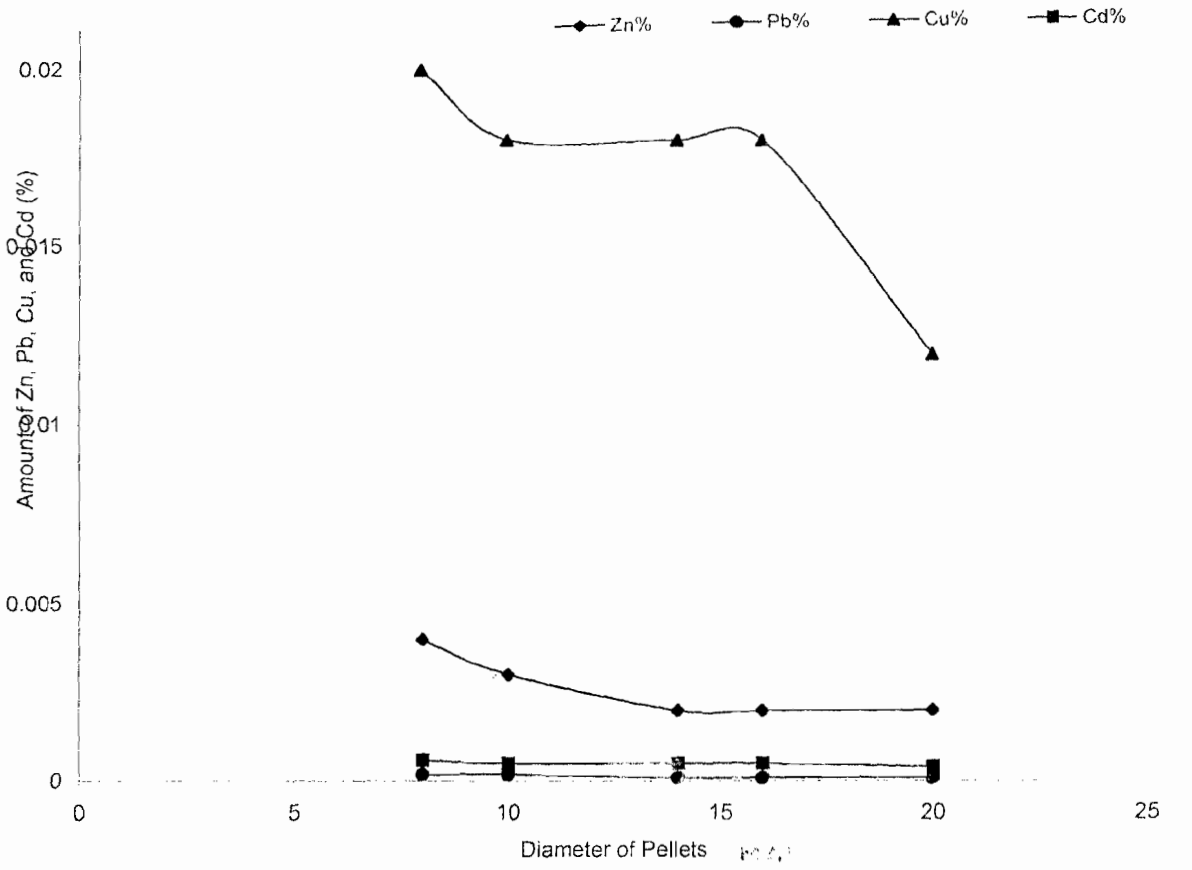


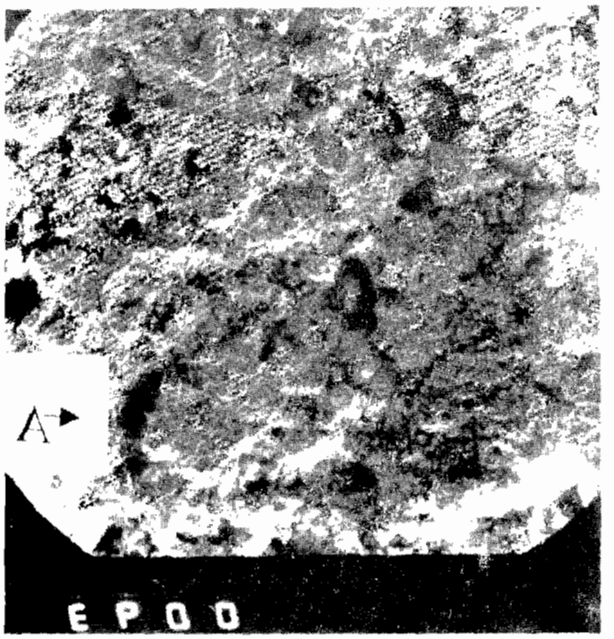
Figure 4: The amount of Zn, Pb, Cu and Cd in reduced pellets versus the diameter of pellets (Reduction time 60min at 1150° C

pellets.

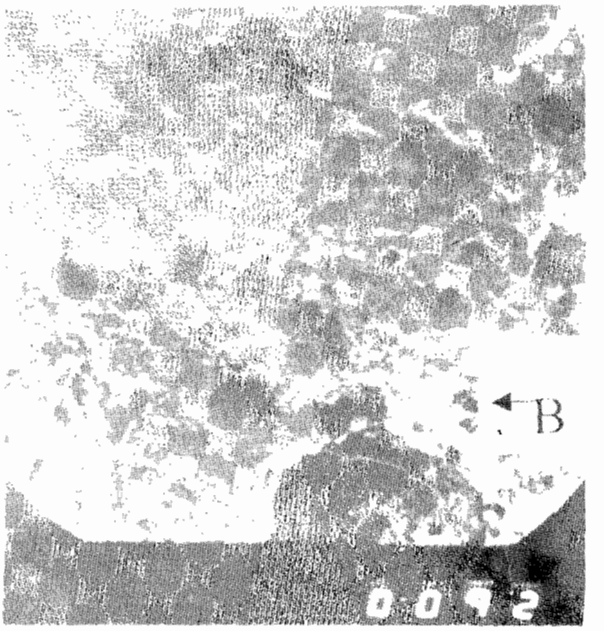
Figure 4 shows the effect of diameter of pellets on the amount of Zn, Pb, Cu. and Cd in reduced pellets. The amount of Zn, Pb, Cd and Cu in reduced pellets is low between pellets diameter 14mm and 20mm. Zn, Pb, Cu and Cd dropped by about 52% between 15mm and 20mm pellets diameter.

Influence of Reduction Temperature, on compressive strengths of reduced pellets.

Table II shows the compressive strengths of the reduced pellets at various temperatures between 600°C and 1200°C. There is a progressive increase in pellet strength with reduction temperature. It may be observed, however, that there is a much higher increase in strength between 1000°C and 1150°C (850 to 970 N/pellet).

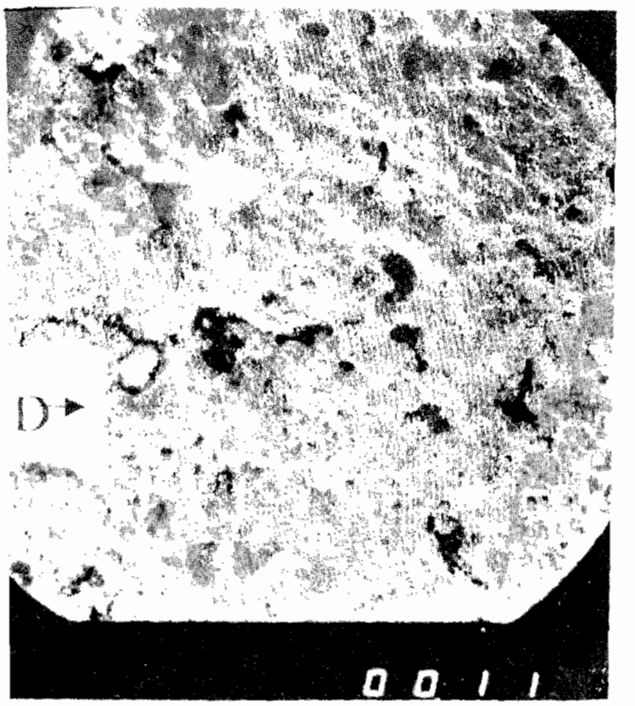


a, pellet diameter P_D = 10mm



b, P_D = 12mm

c, P_D = 14mm



d, P_D = 16mm

Figure 5: Scanning Electron Micrographs of pre-reduced pellets at 1150°C Reduction time, 60mins. -- Composition analyses for points A to D are given in Table III.

a) Reduction temperature 900°C

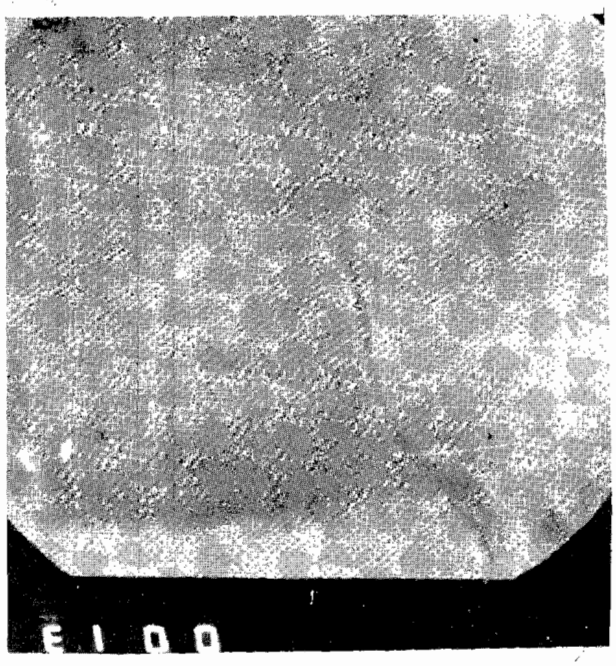
b) Reduction temperature 1000°C

c) Reduction temperature 1150°C

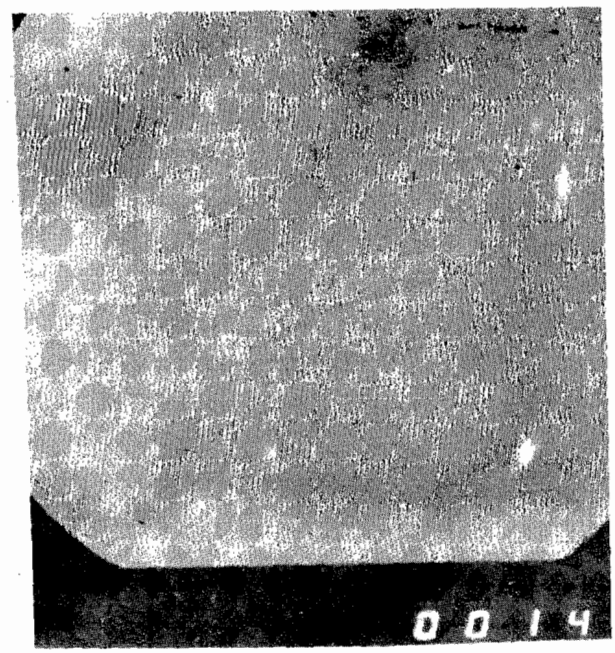
Figure 6: Scanning Electron Micrographs of pre-reduced pellets at various temperatures (Reduction time 60 mins).

Influence of Reduction Temperature on Microstructure.

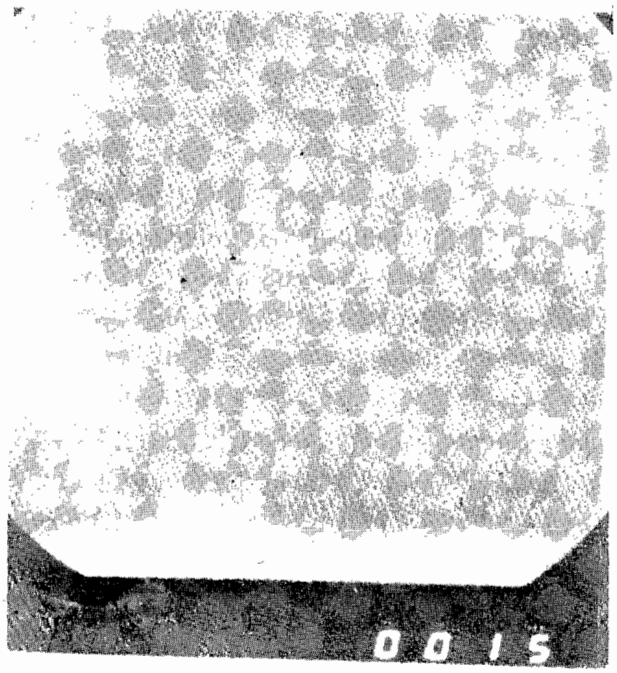
Figure 5 (a – d) represents the scanning electron micrographs of reduced pellets at 1150°C at various pellet diameters. The structures reveal discrete solid particles and some porosities. Table III presents the point analyses for the points indicated in Figures 5 (a – d). The data shows that solid particles which appear light in the fractograph are rich in iron (points A, B, C and D). The scanning electron micrographs of reduced pellets at various temperatures are shown in Figure 6. Figure 7 shows the distribution of Pb, Zn, Cd and Cu in reduced pellets fired at 1150°C.



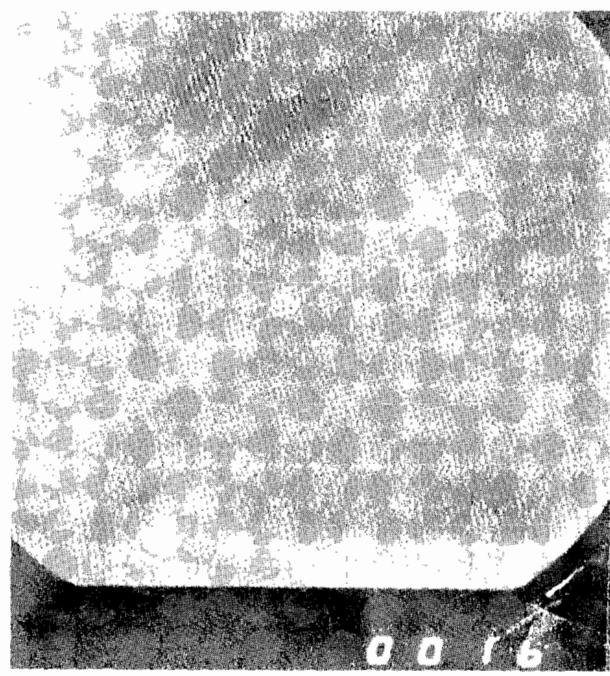
a. Zn



b. Pb



c, Cd



d. Cu

Figure 7: Scanning Electron Micrographs showing the distribution of Zn, Pb, Cd and Cu in pre-reduced pellets

DISCUSSION

Results of this study show that the fracture mode of pellets fired and reduced at high temperatures is clearly transcrystalline. There is also evidence of high melts formation at high temperatures, and a reduction in the number of pores. The intercrystalline fracture path at lower temperatures has given way to transcrystalline fracture at higher temperatures as a result of the development of strong interparticle bonds. These bonds arise primarily from the bonding action of the vitreous gangue melt, as well as from increased interparticle diffusion and the softening and plastic flow processes in solid hematite grains which lead to neck formation and

TABLE III: ELEMENT CONCENTRATION PROFILES SHOWING COMPOSITIONS AT VARIOUS POINTS SHOWN IN FIGURE 4(a), 4(b), 4(c) and 4(d)

Element	Figure 4(a)	Figure 4(b)	Figure 4(c)	Figure 4(d)
	Point A	Point B	Point C	Point D
Fe, %	93.6	92.4	94.9	92.6
Mg, %	4.8	1.2	0.7	1.1
Mn, %	3.6	1.3	2.8	1.2
Al, %	1.1	1.7	0.6	1.4
Si, %	2.3	2.0	2.0	1.6
Ca, %	3.3	0.5	0.4	0.5
P, %	0.03	0.02	0.15	0.02
S, %	0.2	0.15	0.07	0.15
Pb, %	0.002	0.001	0.001	0.002
Zn, %	0.003	0.002	0.002	0.002
Cd, %	0.002	0.002	0.002	0.001
Cu, %	0.010	0.010	0.010	0.010

coalescence of solid particles at contact points. Thus the progressive increase in pellet strength with increased reduction temperature. In reducing Iron oxide balls, reduction commences at the surface and then penetrates the balls basically on a topochemical front. In the presence of a sufficient supply of hydrogen (in this experiment 50cm^3/min.), and as the reduction temperature is increased, reduction penetrates the ball and stronger bonding is developed by the further crystallization and grain growth. The topochemical nature of reduction reaction increases with increasing temperature, indicating that the rate determining process shifts from gaseous diffusion in the pores to solid-state diffusion of ions. During the reduction of hematite to magnetite initially a closely-knit layer of magnetite is formed round the hematite grains, followed by the formation of iron at the gas/magnetite boundary layer by removal of oxygen. This reduction proceeds by the following reaction:

$$4\ Fe_2O_3 + Fe^{2+} + 2e^- \longrightarrow 3\ Fe_3O_4.$$

Fractographic analysis of the edges of the pellet at various points indicate a uniform degree of melting at the edges. This observation is consistent with some previous conclusions reached by Majercak and Asuquo (1977, 2000)

As observed by other investigators (Von Bogdandy and Engell, 2000) porous, open-textured material, with the iron in the form of oxide or ferrite have good reducibility, whereas dense lumps or slaggy material with iron present as silicate will be difficult to reduce. Furthermore, the reduction rate is dependent upon the reduction temperature, reduction time and pellet diameter (figures 2 and 3).

CONCLUSION

The results of this work indicate that major thermal transformation in the iron ore pellets under investigation begin at a temperature of about 1100°C. The scanning electron micrograph of the pellet reduced at 1150°C show evidence of recrystallization of hematite and melting of some gangue components at this temperature. The percentages of Pb, Zn, Cd and Cu in the iron ore pellets were relatively low at the temperature of 1150°C. Compressive strength measurements gave a low strength level (260 N/pellet) for pellets reduced at 600°C, and progressively higher strengths (970 N/pellet) for those fired at 1150°C. At 1150°C, the observed fracture mode was transcrystalline.

From applications point of view, one would conclude from the result of this work that the best reduction temperature for the Nizna-Slana pellets is about 1150°C. Pellets reduced for 60 minutes at this temperature would exhibit high strength, low Pb, Zn, Cd and Cu and considerable porosity (to enhance reducibility during subsequent processing), without precipitating unwanted iron-rich compounds.

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