Progress Report 2

PARTIAL METALLIZATION OF COAL-ADDED PELLETS FOR SMELTING REDUCTION

COLERAINE MINERALS RESEARCH LABORATORY

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By [signature]
Iwao Iwasaki
Senior Research Associate
Endowed Taconite Chair

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University of Minnesota – Duluth
Natural Resources Research Institute
5013 Miller Trunk Highway
Duluth, Minnesota 55811

Coleraine Minerals Research Laboratory
P O Box 188
One Gayley Avenue
Coleraine, Minnesota 55722

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Abstract: In NKK's Duplex-DIOS process, maximum annual productivity is obtained when a DIOS reactor is operated with 30% metallized feed. Laboratory tests were performed to ascertain if 30% metallization could be achieved consistently and with sufficient strength by adding coal less than the stoichiometric requirements. Partially metallized pellets were prepared using an LTV Steel Mining filter cake sample by adding coal in the amount of 35% of the stoichiometric requirements to both unfluxed and fluxed pellets. The optimum temperature of induration was in the range of 1200° to 1300°C. The product analyzed 25 to 30% metallization with compression strengths of 150 to over 300 lb, and apparent densities of 3.4 to 3.5.

INTRODUCTION

NKK's Duplex-DIOS process consists of a rotary hearth furnace (RHF) for pre-reduction followed by smelting reduction in a DIOS reactor. A flowsheet of the Duplex-DIOS process is shown in Figure 1. Figure 2 shows the productivity as a function of %metallization of the feed to the DIOS reactor for a plant of 1,500,000 ton/year. In the figure, it is indicated that pre-reduction to 30% metallization gives maximum annual productivity.

Metallization of coal-added pellets is often mentioned as resulting in low-density and weak products. According to our laboratory tests on magnetic taconite concentrates (see Progress Report No. 1), a coal addition of 100% of the stoichiometric amount was noted to produce 98% metallization and compression strengths of 160 lbs. Lowering of the coal addition to 75% and 50% of the stoichiometric amount led to 87 and 47% metallization, respectively, with compression strengths in excess of 300 lbs in both cases.

When the coal addition was increased even by a few % beyond the stoichiometric amount, the reduced pellets indeed became so weak that compression strengths could not be measured. These observations suggest that it may be easier to achieve low metallization of 30%, not by controlling the reaction time with a stoichiometric addition of coal, but by adding coal in the amount of 35 to 40% of the stoichiometric amounts.

It becomes of interest, therefore, to investigate the possibility of producing partially metallized coal-added pellets by lowering the amount of coal addition to below the stoichiometric addition, and to explore their physico-chemical characteristics for potential application to the Duplex-DIOS process.

In this report, the results of some preliminary tests on partial metallization of coal-added magnetic taconite pellets are summarized.

EXPERIMENTAL

Materials

An LTV Steel Mining filter cake (labeled NRRI-10-00) analyzing 68.1% Fe and 4.32% SiO_2 with 94.9% -200 mesh and a Blaine surface of 2,260 was used. A Pinacle coal analyzing 75% Fixed Carbon and ground to -200 mesh, mentioned in Progress Report No. 1, was used as a reductant. A limestone sample (labeled NRRI-19-98), received from Minntac, was ground to 87% -100 mesh.

The amount of coal addition was fixed at 35% of the stoichiometric amount required to remove oxygen from magnetite in an attempt to achieve 30% metallization. The stoichiometric amount was estimated to be 20% by weight of the magnetic concentrate and coal mixture, based on the fixed carbon content of the coal used. The amount of limestone addition was estimated by making the SiO_2 and CaO balance on the ball mix, so that the basicity of the resulting slag was 1.2.

Methods

Batch balling test and reduction test procedures were the same as in Progress Report No. 1.

RESULTS

Balling Tests

Two series of balling tests were performed, a series of tests without and another series with limestone addition, using 1% bentonite as a binder in both cases. The ball mix composition and ball quality data are presented in Table 1. An addition of limestone lowered the 18" drop number to some extent due presumably to the effects of Ca^{++} and Mg^{++} ions released from the limestone on bentonite, but its effect on dry strength was minimal.

Reduction Roasting Tests

The effects of temperature and of time at each temperature were determined and the results are tabulated in Appendix I. The unfluxed pellets started to decrease their size from 1100°C and the changes became pronounced in the temperature range of 1200° to 1250°C with attendant increase in compression strengths. With fluxed pellets, the volume decreased throughout the temperature range tested, due presumably to calcination of the limestone. The volume change was even more pronounced in the temperature range of 1200° to 1250°C, again with attendant increase in compression strengths.

Figure 3 summarizes the relationship between volume decrease and compression strengths upon reduction roasting in the temperature range of 1200° to 1300°C for time at temperature of 4 to 16 minutes. It is evident that reasonably good correlation can be observed between compression strengths and volume decrease, and fluxed pellets lead to more pronounced volume decrease.

Volume decrease upon reduction suggests an increase in apparent densities, which would be beneficial in penetrating the slag layer in injection smelting. Accordingly, apparent densities of the pellet samples were estimated from average diameters and weights of individual pellets. Results are listed in Table 2. With increasing reduction temperature, the apparent densities increased from 2.8-2.9 for dried balls to 3.4-3.5 for reduced pellets at 1200°-1250°C, roughly paralleling the volume decrease.

The effects of reduction temperature on %metallization and compression strengths of reduced pellets are shown in Figure 4. Percent metallization increased with the reduction temperature, approaching 30% metallization in the temperature range of 1200° to 1300°C. Compression strengths also increased, reaching 150 to 350 lb in the said temperature range.

To investigate the nature of iron species, x-ray diffraction patterns were obtained, and the results are shown in Figures 5 and 6. Wustite (FeO) and metallic iron (Fe) are seen to be the major phases, with magnetite (Fe_3O_4) peaks disappearing above 1100°C. Quartz (SiO_2) peaks also disappeared above 1150°C, and, in the case of unfluxed pellets, led to fayalite (Fe_2SiO_4) formation. Fayalite peaks started to appear at as low as 1000°C and became progressively stronger as the temperature was raised. In fluxed pellets, monticellite ($CaMgSiO_4$) was the product, and the peaks became recognizable at 1150°C and became stronger as the temperature was raised.

Figures 7 and 8 show the photomicrographs of unfluxed and fluxed pellets, respectively, at different temperatures. The microstructures show that both slag and wustite phases are beginning to recrystallize with globules of metallic iron distributed throughout the matrix. The metallic iron globules are seen to increase their size with temperature.

In Figure 9, the effects of coal addition levels on %metallization and compression strengths are summarized, incorporating the results at coal addition levels of 50, 75, 100, 110 and 125% of the stoichiometric amount (9.5, 14, 19, 22 and 25% by weight) reported. It is readily apparent that coal additions beyond the stoichiometric amount had devastating effect on compression strengths.

SUMMARY

Low metallization of 30%, the level NKK reported to show maximum annual productivity in their RHF-DIOS combination, may be achieved by adding coal in the amount of 35 to 40% of the stoichiometric amount and heating to 1200° to 1300°C in an

inert atmosphere. The pre-reduced pellets thus produced have 150 to over 300 lb compression strengths, with apparent densities of 3.4 to 3.5. It is expected that the product will be suitable for injection through molten and foaming slag layer in DIOS reactors.

At this level of metallization and temperature, no serious sticking problem was observed during reduction. These observations suggest a possibility of producing pre-reduced pellets in an RHF with greatly improved productivity, and also of using, for example, even a shaft furnace for pre-reduction. It becomes of interest to assess their relative merits in producing pre-reduced pellets for use in the DIOS reactor.

In this investigation, a currently produced magnetic concentrate with over 4% SiO_2 and a somewhat excessive amount of bentonite was used as a starting point. It is necessary to test how lowering of SiO_2 to 3 or 2% or even less, and lowering the amount of bentonite or its substitute may affect the physico-chemical properties of the partially metallized products. It becomes of interest then to arrive at an optimum SiO_2 level of concentrates whereby a combination of beneficiation and smelting attains the overall minimum cost.

Table 1. Ball Quality Using LTV Filter Cake

Test No.	Ball Mix Composition, %				Ball Quality				
	Mag. Conc.	Limestone	Coal	Bentonite	Wet 18" Drop	Wet Str. lb	% Moist.	Dry 18" Drop	Dry Str. lb
104	92	---	7[(2)]	1	10	2.6	10.3	1	7.4
105	83.5	9.2[(1)]	6.3[(2)]	1	7.8	2.7	10.3	1	7.6

(1) $CaO + MgO / SiO_2 = 1.2$
(2) 35% of stoichiometric addition

Table 2. Effect of Temperature on Apparent Densities of Coal-added Pellets

Coal Addition: 35% of stoichiometric amount
Time at Temperature: 8 minutes

Temp °C	Apparent Density	
	Unfluxed (Mix 104)	Fluxed (Mix 105)
Dried	2.9	2.8
1000	2.8	---
1100	2.9	2.6
1150	2.9	2.5
1200	3.3	3.2
1250	3.4	3.5
1300	---	3.4

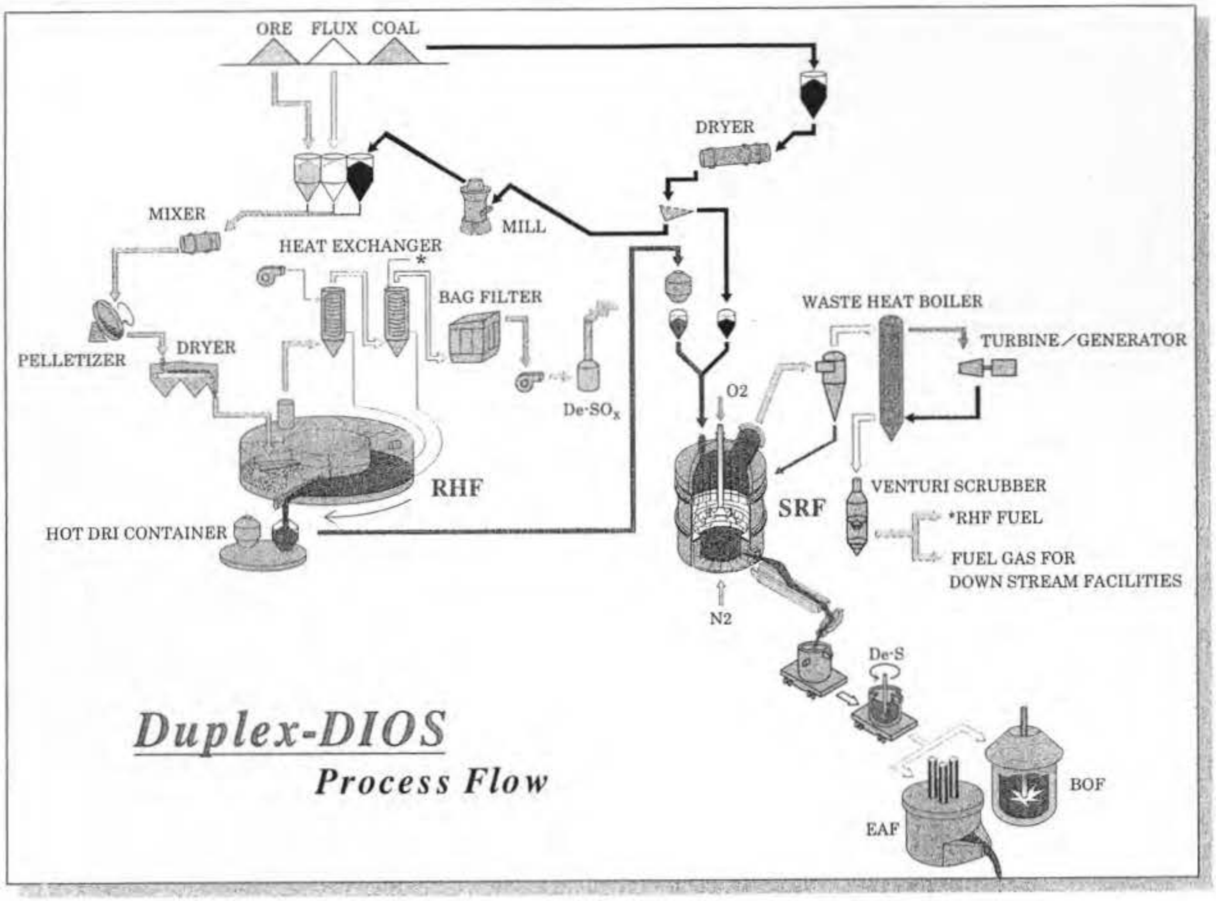

Figure 1. Flowsheet of NKK Duplex-DIOS Process

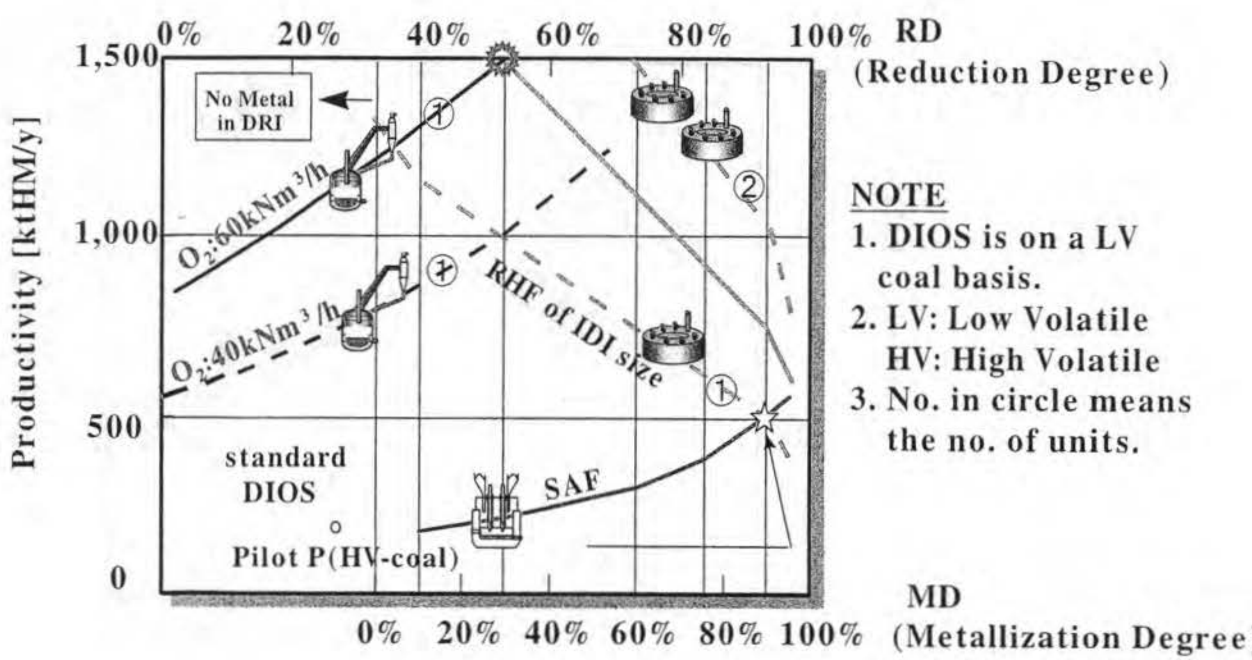

Figure 2. Effect of Metallization Degree on Productivity of Duplex DIOS Process

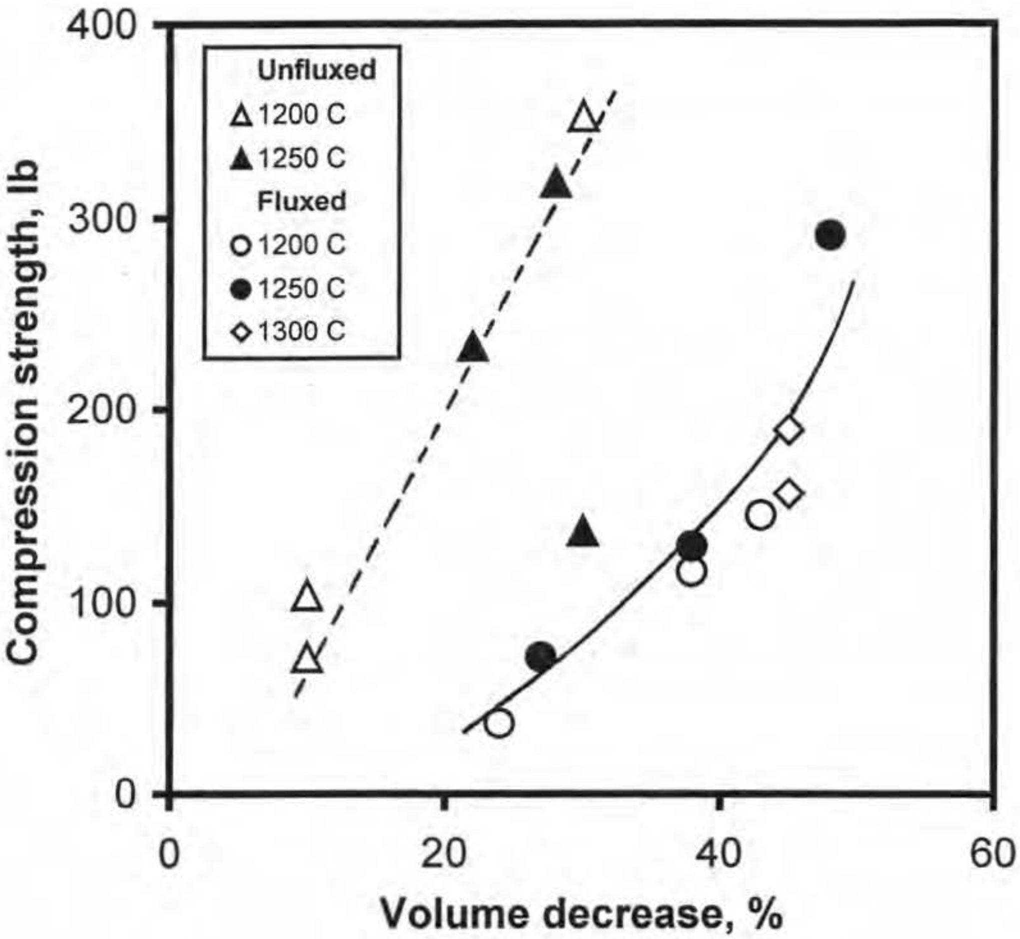

Figure 3. Relationship between Volume Decrease upon Reduction Roasting and Compression Strengths of Metallized Pellets

Time at temperature varied from 4 to 16 minutes

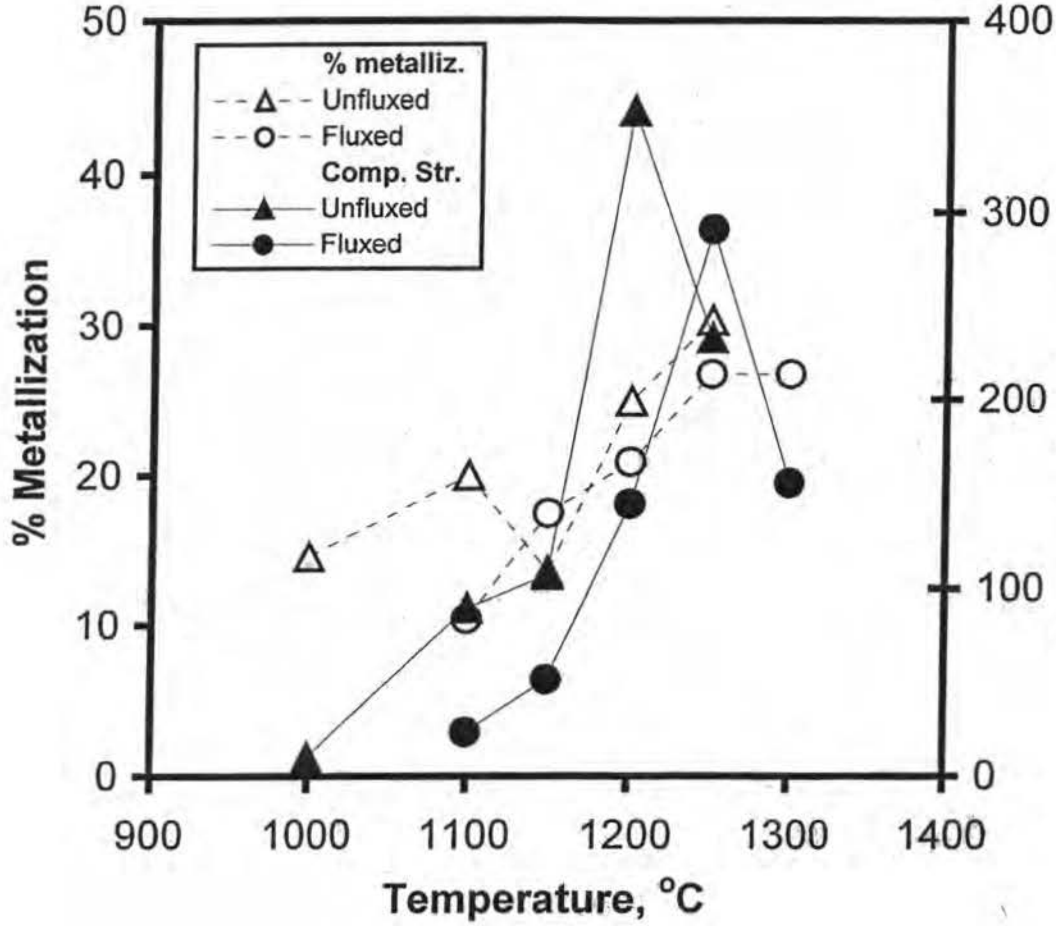

Figure 4. Effect of Temperature on %Metallization and Compression Strengths
Time at temperature: 16 minutes

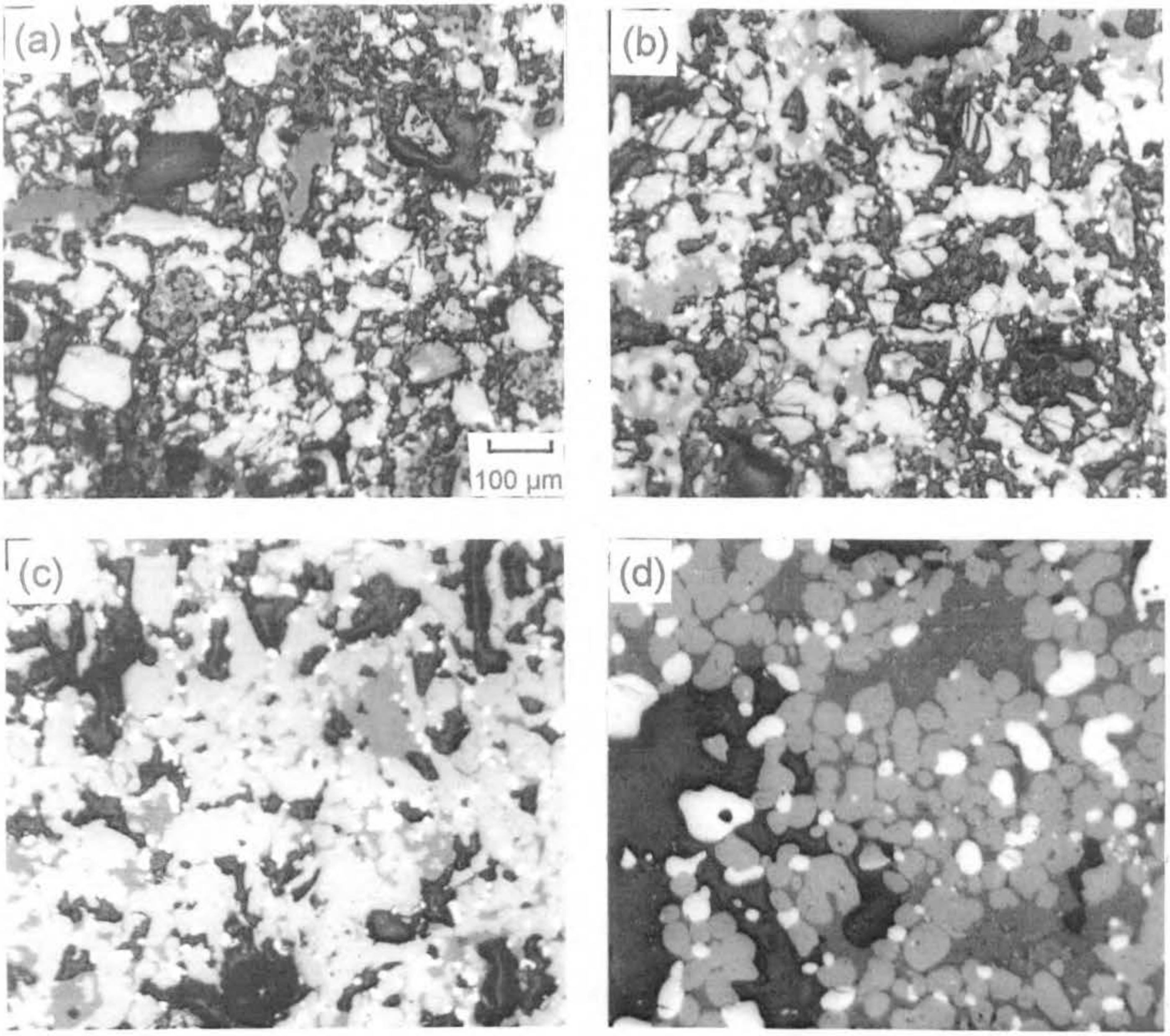

Figure 5. Effect of Temperature on Metallization of Unfluxed, Coal-Added Pellets (Mix 104)

Time at temperature: 16 minutes

(a) 1100°C
(b) 1150°C
(c) 1200°C
(d) 1250°C

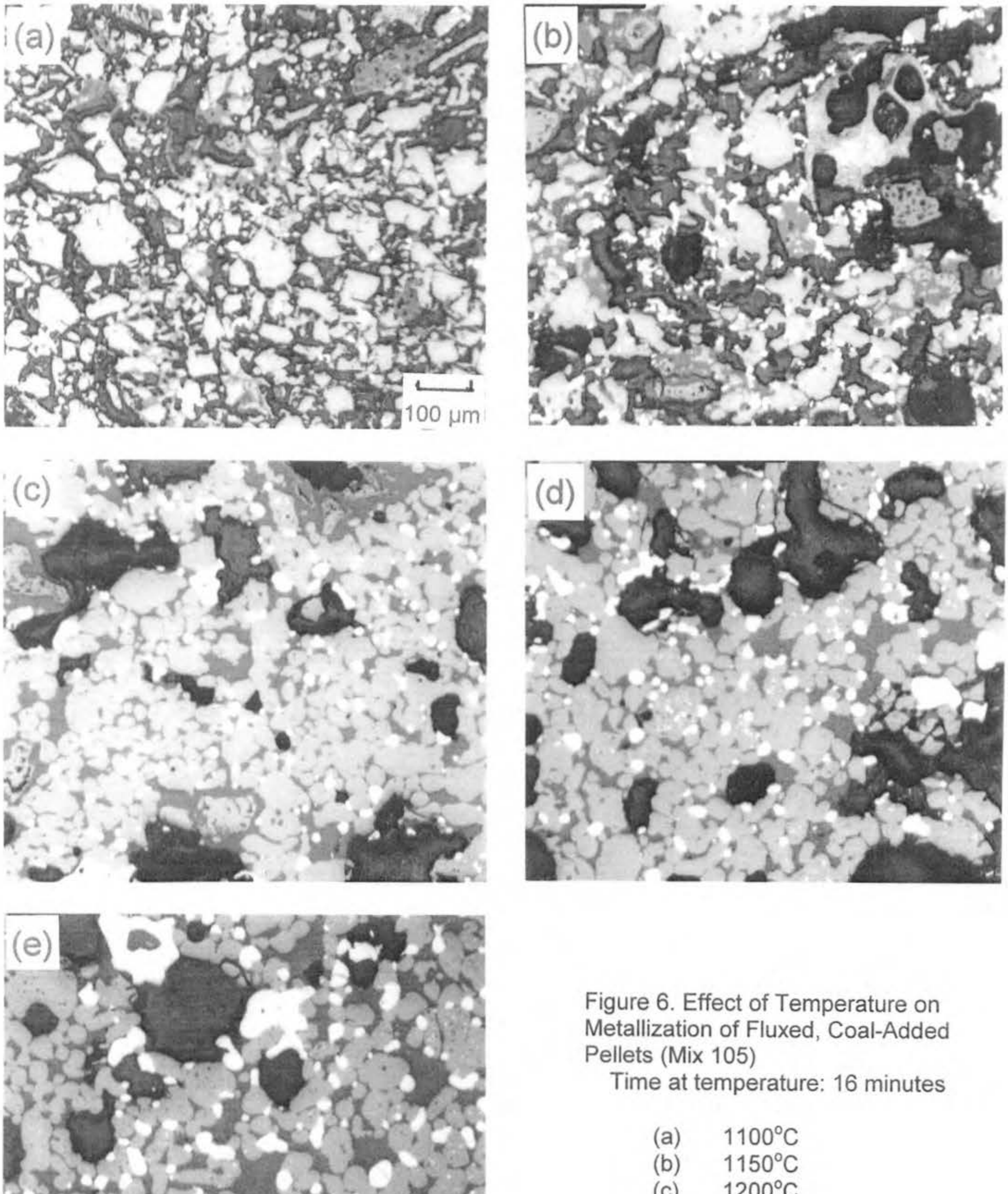

Figure 6. Effect of Temperature on Metallization of Fluxed, Coal-Added Pellets (Mix 105)
Time at temperature: 16 minutes

(a) 1100°C
(b) 1150°C
(c) 1200°C
(d) 1250°C
(e) 1300°C

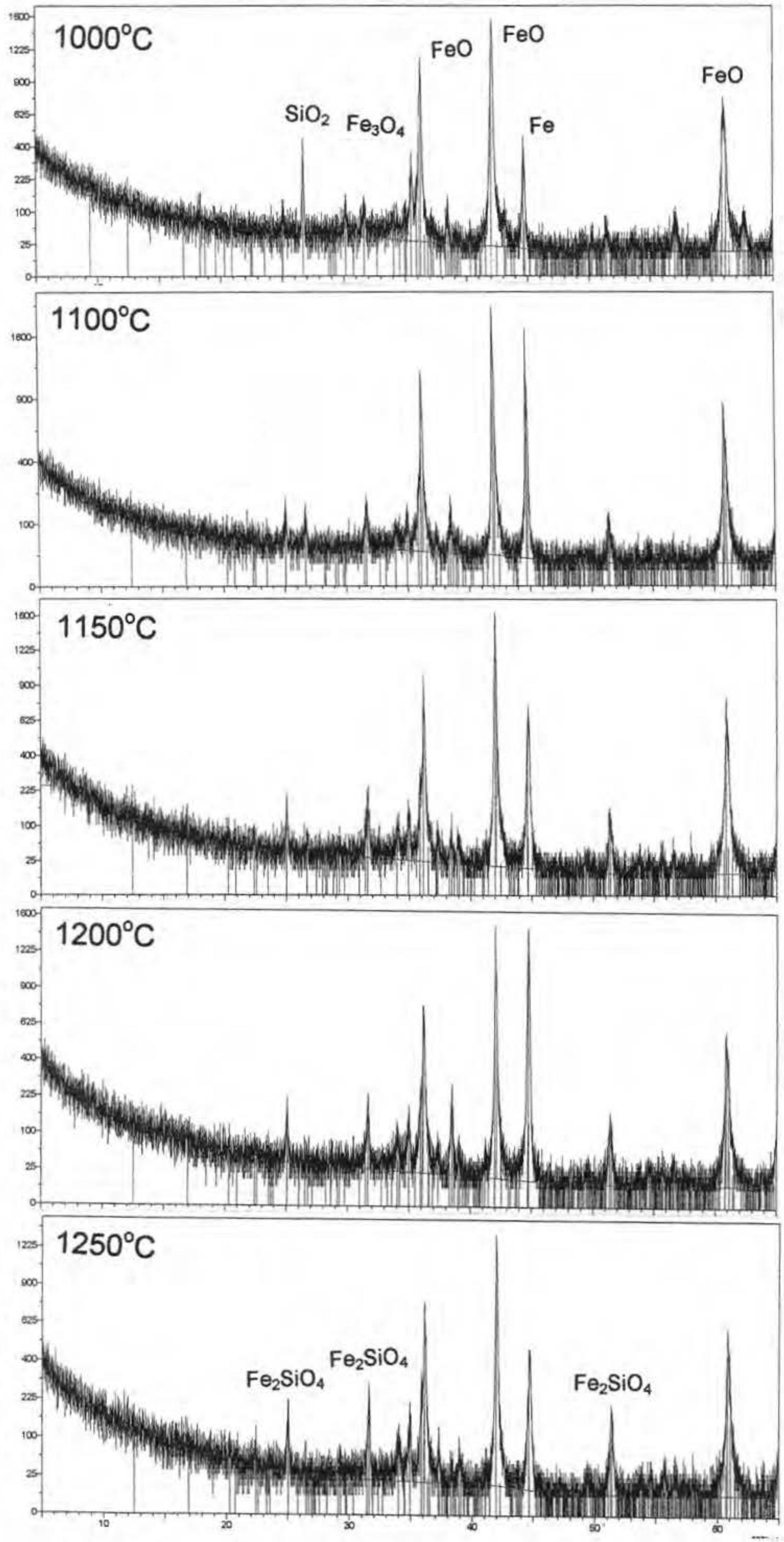

Figure 7. X-ray Diffraction Patterns of Unfluxed Pellets Showing the Effect of Reduction Temperature

Time at temperature: 16 minutes

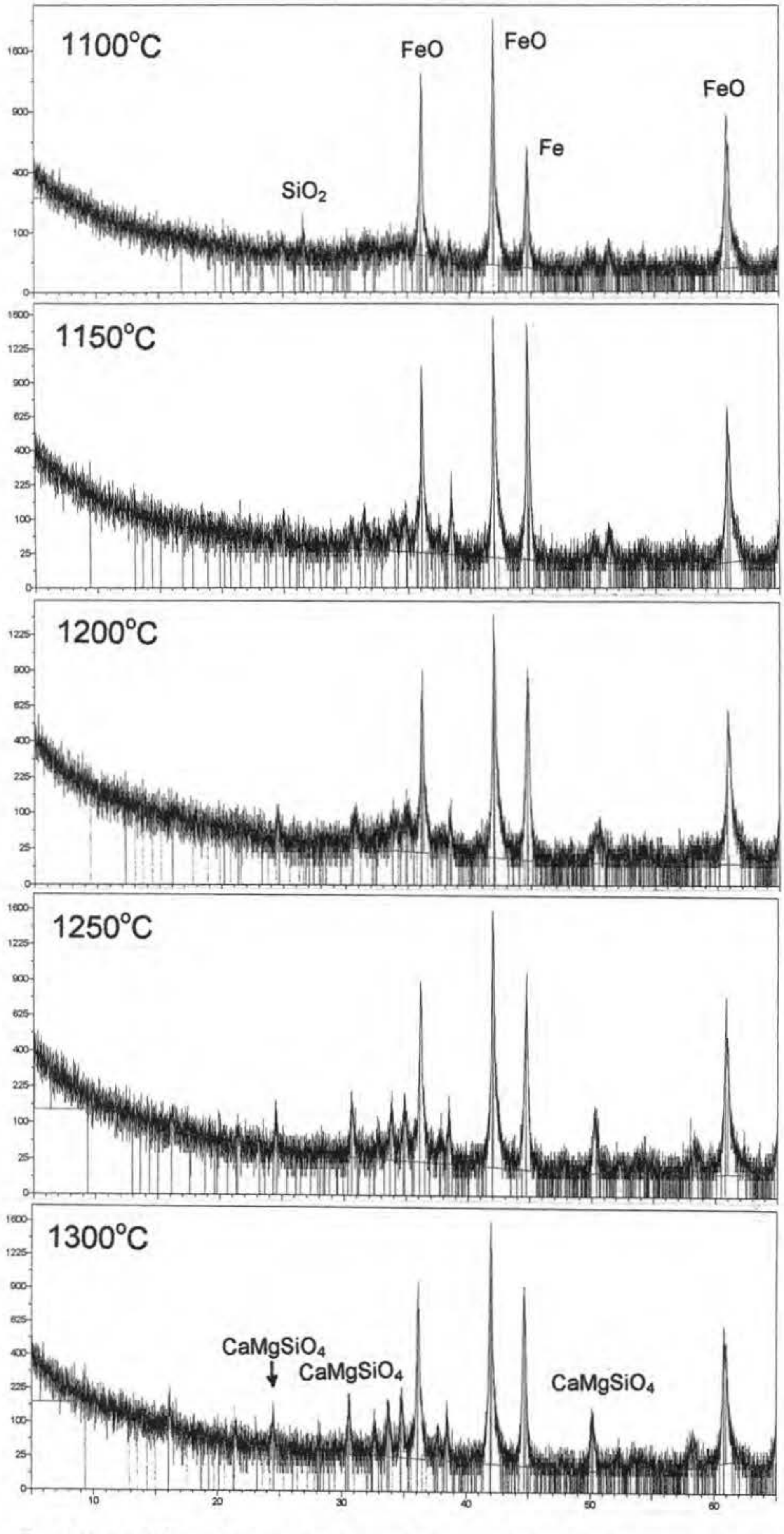

Figure 8. X-ray Diffraction Patterns of Fluxed Pellets Showing the Effect of Reduction Temperature

Time at temperature: 16 minutes

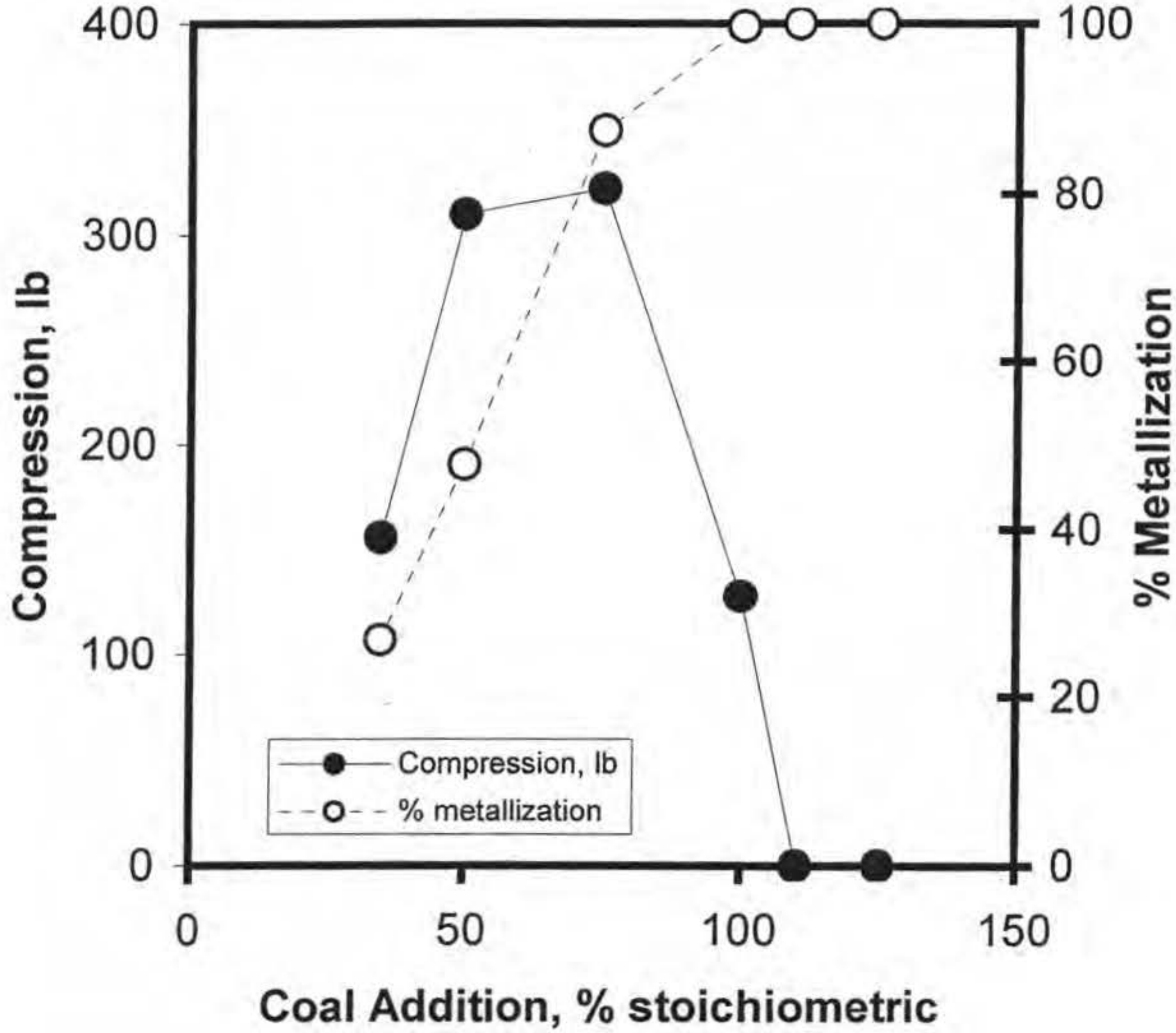

Figure 9. Effect of Coal Addition Levels on %Metallization and Compression Strengths of Metallized Pellets
Reduction temperature: 1300°C

Appendix 1.

Reduction test results showing the effects of temperature and time at temperature with coal addition of 35% of stoichiometric requirement

Temp °C	Time at temp., min.	Diameter, mm		Vol. Change %	Compression lb	% Metalliz.
		Before	After			
Mix 104 (Unfluxed)						
1000	4	11.6	11.8	0	10	---
	8		11.5	0	15	---
	16		11.9	0	10	14.6
1100	4		11.9	0	13	---
	8		11.4	-5	43	---
	16		11.0	-15	89	20.0
1150	4		11.5	-3	29	---
	8		10.9	-17	85	---
	16		10.7	-22	107	13.6
1200	4		11.2	-10	72	9.5
	8		11.2	-10	104	19.3
	16		10.3	-30	353	24.9
1250	4		10.3	-30	137	15.7
	8		10.4	-28	319	25.2
	16		10.7	-22	233	30.3
Mix 105 (Fluxed*)						
1100	4	12.8	12.3	-11	10	---
	8		12.4	-9	14	---
	16		12.0	-18	23	10.4
1150	4		12.3	-11	20	---
	8		12.0	-18	33	---
	16		11.6	-26	51	17.5
1200	4		11.7	-24	37	8.9
	8		10.9	-38	116	19.2
	16		10.6	-43	145	20.9
1250	4		11.5	-27	72	24.6
	8		10.9	-38	129	30.4
	16		10.3	-48	291	26.7
1300	4		10.5	-45	189	23.7
	16		10.5	-45	156	26.7

*$CaO / SiO_2 = 1.2$