

Production of Fine ZnO Powders by Carbothermal Reduction

Heon-Jin Choi, June-Gunn Lee, Kwang-Taik Jung* and Kihwan Kim*

Division of Ceramics, Korea Institute of Science and Technology,
P.O. Box 131, Cheongryang, Seoul 130-650, Korea

*Hanil Zinc Oxide Industrial Co., Ltd., #1NA-803, Sihwa Ind. Complex,
Kyungki-Do 429-450, Korea

(Received August 25, 1998)

Carbothermal reduction has been one of the important processes for the production of ceramic raw materials such as silicon carbide, silicon nitride, boron carbide, etc. The process has also been one of several trials for the recovery of ZnO from ZnO-containing waste. It usually involves two consecutive steps: the evolution of Zn vapor and its oxidation with air. In this study a ZnO-containing raw material is reduced by carbon at 1250°C and the evolved Zn vapor is oxidized with air, resulting in fine powders of ZnO. Computer programs, THERMO and PYROSIM developed by MINTEK, are used to simulate the process thermodynamically and the results are compared with the experimental results. It is shown that the ZnO-containing raw material can be reduced and can form fine ZnO with the yield as high as 98.7% under a proper condition. Based on these results, a process is engineered for the production of ZnO in a rotary kiln at a rate of 3 tons/day. The produced ZnO powders show properties suitable to the usual applications in ceramic industries with a purity of > 95wt% and an average particle size of ~3 μm.

Key words : ZnO, Carbothermal reduction, Simulation, Rotary kiln

I. Introduction

The carbothermal reduction has been used in many fields such as ablation in rocket nozzle, ore processing, and synthesis of carbides, and nitrides in powder or whisker form. It is well recognized that the reaction involves many steps and substeps.

In ceramics field, systematic studies were first carried out by a series of works¹⁻⁹⁾ on the carbothermal reduction of SiO₂ by Lee and Cutler. They recognized the gas-solid reaction as the main reaction mechanism and the effectiveness of Fe as catalyst.

Further study by Choi and Lee¹⁰⁾ on the formation of SiC whiskers by the carbothermal reduction of SiO₂ proposed the gas-gas reaction that involved a two-step reaction scheme. First, SiO vapor was generated via the carbothermal reduction of silica. Second, the generated SiO vapor was reacted with the C-carrying vapors such as CO and CH₄ which results the growth of SiC in whisker form.

They also confirmed that an alternative route, the gas-liquid-solid mechanism at the presence of Fe liquid was the preferred method for the efficient formation of SiC whiskers. Here, the Fe drops acted as the reservoir of SiO vapor and controlled the diameters of SiC whiskers.

ZnO is an important ingredient for ceramic products such as varistors, ferrites, frits, pigments, etc. It is produced via various routes¹¹⁻²⁴⁾ that include the carbothermal reduction (The American Process) and the direct oxidation of Zn vapor (The French Process).

It is well documented that the reduction of ZnO occurs via two consecutive gas-solid reactions:²¹⁾



The evolved Zn vapor can be oxidized with air via the gas-gas reaction that is capable of producing fine powders of ZnO:



For the last 10 years, much effort has been exerted to achieve the recycling of Zn via the carbothermal reduction of steel mill dust that amounts to several million tons every year worldwide. Therefore, various patents, in which systems such as a rotary kiln,¹⁶⁻¹⁹⁾ lance reactor,¹¹⁻¹³⁾ plasma reactor,¹⁴⁻¹⁵⁾ etc. were employed, have been disclosed on this field.

The main stimulants for these activities are to meet the environmental protection regulations as well as to recover valuable sources such as Zn, Pb, Fe, etc. The following are some typical descriptions of processes that involve operation in a rotary kiln.

United States Patent 5,547,490 by Discher *et al.*¹⁹⁾ describes a method and installation for removing lead and zinc from foundry dust. In this patent, the foundry dust is fed to a first furnace atmosphere which is preferably at 1000~1100°C. With the dust pellet being continuously rolled around, it remains therein until chlorine, alkali, and lead compounds have almost completely evaporated

out of the dust.

A reducing agent, in particular coal, is then introduced into the foundry dust and is fed to a next furnace atmosphere which is at 1150~1350°C, where it is continuously rolled around. In that way the ZnO contained in the dust is reduced and Zn vapor is formed. And the Zn vapor is transferred into the oxygen-bearing furnace atmosphere where the formation of ZnO takes place.

United States Patent 4,673,431 by Bricmont¹⁸⁾ describes a furnace dust recovery process. In this patent, pellets are formed from the waste dust and dried to permit charging in an oxidation chamber wherein an oxidizing atmosphere is maintained. The chamber is heated to a temperature sufficient to vaporize oxide of lead and, if present, also oxides of cadmium, potassium, and sodium. The vapor is cooled and separated from furnace gas.

The residual mass is cooled after removal from the oxidation chamber and fed into a reduction chamber wherein a reducing atmosphere is maintained. The reduction chamber is heated to a temperature of 982~1093°C to reduce ZnO and form Zn vapor which is cooled and separated from the furnace gas.

United States Patent 4,983,214 by Bottinelli *et al.*¹⁷⁾ describes a method and apparatus for direct reduction of metal oxides. In this patent, a first burner is used for drying, preheating, and calcining the pellets made of Zn-containing waste within the first chamber. A second chamber within the kiln, having a diameter greater than the first chamber, is used for reducing the pellets with heat supplied from a second burner. The axial angle of the kiln is varied to regulate the flow rate of the pellets from the first chamber to the second.

In this study a ZnO-containing raw material is reduced by carbon at 1250°C and the evolved Zn vapor is oxidized with air, resulting in fine powders of ZnO. Computer programs, THERMO and PYROSIM developed by MINTEK,¹⁰⁾ are used to analyze and to simulate the process thermodynamically and the results are compared with the experimental results.

PYROSIM is a general-purpose computer program for the steady-state simulation of pyrometallurgical processes that is based on the principle of minimizing the Gibbs free energy of the system under consideration. The program involves a variety of models to predict the flow rate, product composition, and distribution of elements between phases. One of the primary strengths of the program is its built-in capability to calculate multi-component multi-phase equilibria, along with the automatic evaluation of mass- and energy-balance.

This study, which involves both the simulation and its experimental confirmation, will provide a valuable database and simulation format for the industries that treat Zn-containing waste. The differences in composition and operational condition of waste material do not pose any problem since some simple adjustments in input data are all needed to utilize these results.

Table 1. The Raw Materials Used in this Study

Raw Material	Composition (wt%)	Grain Size (mesh)	Remarks
ZnO-Ash	ZnO 60, Zn 40	-45	similar to ash from galvanizing process
Cokes	C 88, Ash 12	-14+60	similar to combustion gas from LNG
Gas Mixture	N ₂ 80 vol%, H ₂ O 12 vol%, CO ₂ 8 vol%	-	
LNG	Hydrocarbons>99	-	commercial grade

II. Experimental

1. Thermodynamic Analysis

For the preliminary evaluation of the system described by Eqs. (1), (2), and (3), a computer program THERMO is used to analyze the process thermodynamically.

2. Reduction Test

The raw materials used in this study are listed in Table 1. It can be seen that each raw material is carefully chosen so that it is as close as possible to the actual materials used on site. For example, ZnO-ash has not only ZnO but also metallic Zn as a major phase.

Samples were prepared by mixing 1 g of ZnO-ash with 0~1 g of cokes in a shaker. It was placed into the hot zone of an alumina tube furnace and the gas mixture shown in Table 1 was introduced into the tube. Then the furnace was heated to 1250°C at a rate of 625°C/h and was held for predetermined periods of time.

The weight loss was monitored after each period of time and the composition of the remaining residue was chemically analysed to confirm the degree of reduction that represents the yield of Zn_⊙.

3. Simulation for the Pilot-plant Operation

A computer program, PYROSIM, is used to simulate the pilot-plant operation thermodynamically.

4. Pilot-plant Test

A rotary kiln (ID=1 m, length=2 m, rotation=0.5 rpm) with a lining of magnesia-chromia refractory was used for the pilot-plant production of Zn_⊙ from ZnO-ash. LNG (liquid natural gas) was the source of heat that kept the operation temperature at 1250°C. The evolved Zn_⊙ was converted to ZnO powders with air in an oxidation chamber attached next to the rotary kiln.

Chemical composition, microstructure, and particle size of the produced ZnO powders were analyzed to assure the feasibility of the operation. The overall Zn recovery from the ZnO-ash was assessed from the amount of ZnO powders collected in a baghouse and from the amount of Zn and ZnO remained in slag.

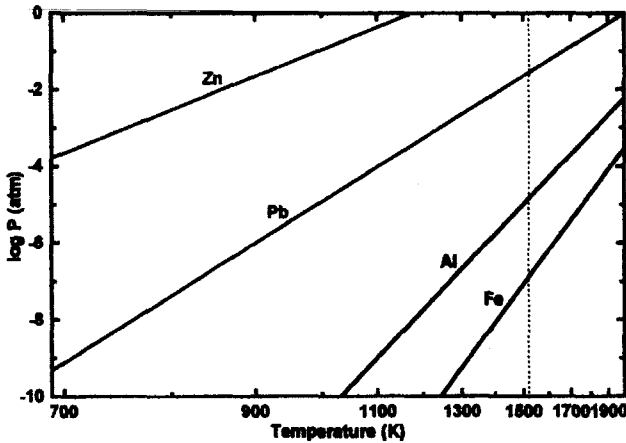


Fig. 1. Equilibrium vapor pressures of various metals that usually exist in a Zn-containing waste.

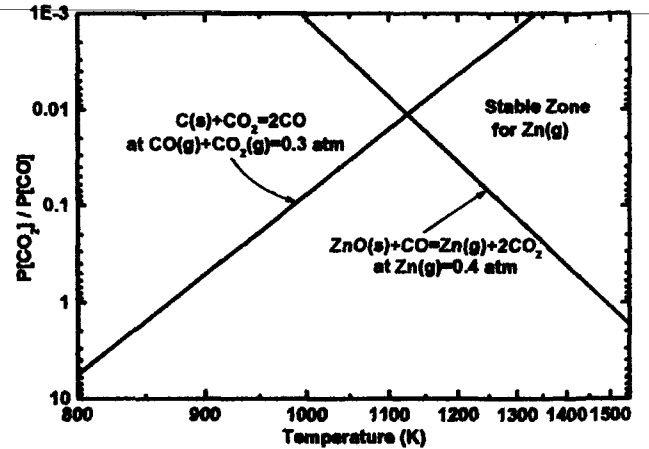


Fig. 2. Stable zone for the formation of $Zn_{(g)}$ in the ZnO-C system.

III. Results and Discussion

1. Thermodynamic Analysis

When the prepared sample (mixture of ZnO-ash and cokes) is heated to 1250°C, it is expected that the evaporation of metallic Zn takes place first:



Fig. 1 shows the equilibrium vapor pressures of various metals, which usually exist in Zn-containing waste, obtained from THERMO. It shows that the driving force for evaporation increases in the order of $Zn > Pb > Al > Fe$, which implies the relative easiness of Zn evaporation at the expected operation temperature of 1250°C (1523K, the vertical dotted line in Fig. 1). It is, therefore, expected that Pb might have some tendency to evaporate along with Zn while Al and Fe should remain as solid in the form of slag.

As indicated in Eqs. (1) and (2), the reduction of ZnO by C at a given temperature is a function of the partial pressures of CO and CO_2 . Fig. 2 shows the stable zone for the formation of $Zn_{(g)}$ obtained from THERMO assuming: $P_{Zn(g)}=0.4$ atm, $P_{CO}+P_{CO_2}=0.3$ atm, and $P_{N_2}=0.3$ atm. It is clearly shown that $Zn_{(g)}$ can be formed in a relatively wide range of P_{CO_2}/P_{CO} ratio ($1 \sim 10^{-4}$) at the expected operation temperature of 1250°C (1523K).

2. Reduction Test

The reduction test was carried out to determine whether or not direct heating with LNG is feasible for the reduction of ZnO-ash in a rotary kiln. Hence, a gas mixture similar to the combustion gas from LNG was used for the test. Fig. 3 shows the results of the test carried out in a alumina tube furnace described in Section II.

There is a general trend that the $Zn_{(g)}$ yield increases with the carbon addition, which is a well known phenomenon in the field of carbothermal reduction. As indicated as a solid curve in Fig. 3, the $Zn_{(g)}$ yield reaches as high

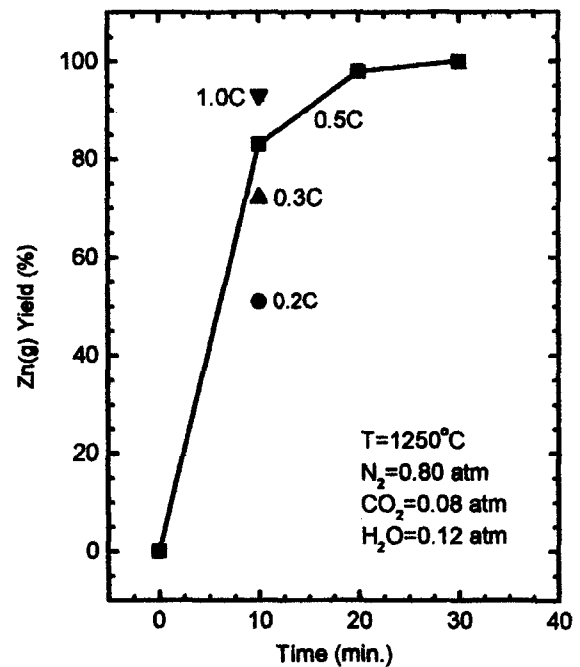


Fig. 3. Reduction kinetics of ZnO-ash by C.

as 98.7% in 30 min. for the sample with 0.5 g of C. This implies that both metallic Zn and ZnO in the sample have transformed to $Zn_{(g)}$ by evaporation and reduction, respectively.

3. Simulation for the Pilot-plant Operation

In the rotary kiln under consideration, several reactions are taking place at the same time such as combustion of LNG, evaporation of metallic Zn, and reduction of ZnO. Furthermore, it is expected that there exists some difference of gas composition between outside and inside of the batch since the true equilibrium is never set in a rotary kiln.

Outside of the batch, the combustion of LNG takes

place and N_2 , CO_2 , and H_2O will be the dominant gas species with some dilution from the product gases from the batch. Inside of the batch, on the contrary, the evaporation of metallic Zn and the reduction of ZnO takes place and $Zn_{(g)}$ and CO will be the dominant gas species with some dilution from the combustion gas. Simulations are done with PYROSIM considering for both cases and for the overall process.

Table 2 shows the simulated result for the reduction of

ZnO-ash under the outside atmosphere of the batch. Here, the atmosphere of 'comb gas' is assumed to have 0.16 wt% CO, 14.99wt% CO_2 , 0.01wt% H_2 , 12.40wt% H_2O , and 72.44wt% N_2 that is the typical composition of combustion gas from LNG.

The result can be summarized as follows: when 3.2 kg/h of ZnO-ash and 0.5 kg/h of cokes are mixed and are fed into a rotary kiln with 21.6 kg/h of 'comb gas', 2.8 kg/h of $Zn_{(g)}$ (see Table 2, product gas 25.21 kg/h \times Zn gas content

Table 2. Simulated Result for the Reduction of ZnO-ash under the Outside Atmosphere of the Batch at Heat Loss=0, T=1250°C, and $P_{total}=1$ atm

FEED	FLOW RATE (kg/h)		T (°C)						
ZnO-ash	3.20		25						
cokes	0.50		25						
'comb gas'	21.6		1250						
PRODUCT									
gas	25.21		1250						
slag	0.09		1250						
ENERGY									
requires 4.23 kWh/h (15.2 MJ/h) including a rate of energy loss of 0 kWh/h.									
ANALYSES (wt%)									
FEED	C	CO	CO_2	$H_2O_{(g)}$	N_2	SiO_2	$Zn_{(g)}$	ZnO	Zn
ZnO-ash	--	--	--	--	--	0.01	39.99	60	--
cokes	88	--	--	--	--	12	--	--	--
'comb gas'	--	0.16	14.99	12.40	72.44	--	--	--	--
PRODUCT									
gas (vol%)	--	3.85	9.07	15.15	64.77	--	4.96	--	--
gas	--	3.69	13.66	9.34	62.06	--	11.10	--	--
slag	--	--	--	--	--	68.39	--	26.61	5.00

*Minor phases less than 3wt% are deleted from the table.

Table 3. Simulated Result for the Reduction of ZnO Waste Inside of the Batch at Heat Loss=0, T=1250°C, and $P_{total}=1$ atm

FEED	FLOW RATE (kg/h)		T (°C)						
ZnO-ash	3.20		1250						
cokes	0.50		1250						
'batch gas'	6.00		1250						
PRODUCT									
gas	9.39		1250						
slag	0.31		1250						
ENERGY									
requires 2.64 kWh/h (9.51 MJ/h) including a rate of energy loss of 0 kWh/h.									
ANALYSES (wt%)									
FEED	C	CO	CO_2	$H_2O_{(g)}$	N_2	SiO_2	$Zn_{(g)}$	ZnO	Zn
ZnO-ash	--	--	--	--	--	0.01	39.99	60	--
cokes	88	--	--	--	--	12	--	--	--
'batch gas'	--	24	6	--	30	--	40	--	--
PRODUCT									
gas (vol%)	--	39.28	--	--	27.63	--	33.09	--	--
gas	--	27.25	--	--	19.17	--	53.59	--	--
slag	18.96	--	--	--	--	19.49	--	--	61.55

*Minor phases less than 1wt% are deleted from the table.

11.1 wt%) will form from the evaporation of metallic Zn and from the reduction of ZnO if 4.23 kWh/h (15.2 MJ/h) of heat is supplied. It also indicates that 0.0045 kg/h of metallic Zn (see Table 2, product slag 0.09 kg/h \times Zn content 5 wt%) and 0.02 kg/h of ZnO (see Table 2, product slag 0.09 kg/h \times ZnO content 26.61 wt%) will remain in slag as a solid.

Table 3 shows the simulated result for the reduction of ZnO-ash under the inside atmosphere of the batch. Here, it is assumed that the process is under the semi-steady state and both the reactants and products are at a constant temperature of 1250°C. The atmosphere of 'batch gas' is also assumed to have 24 wt% CO, 6 wt% CO₂, 30 wt% N₂, and 40 wt% Zn_g.

The result can be summarized as follows: when 3.2 kg/h of ZnO-ash and 0.5 kg/h of cokes are mixed and are fed into a rotary kiln with 6 kg/h of 'batch gas', 2.63 kg/h of new Zn_g (see Table 3, gas product 9.39 kg/h \times Zn gas content 53.59wt%-'batch gas' feed 6 kg/h \times Zn gas content 39.99 wt%) will form from the evaporation of metallic Zn and from the reduction of ZnO if 2.64 kWh/h (9.51 MJ/h) of heat is supplied. It also indicates that 0.19 kg/h of Zn (see Table 3, product slag 0.31 kg/h \times Zn content 61.55 wt%) will remain in slag as a solid.

The above results indicate that Zn_g can be formed with minimal formation of slag at two different atmospheres (one oxidizing and the other reducing) at the presence of C at temperature of 1250°C. The next step, the oxidation of Zn_g, is not considered here since its spontaneous nature is well known if sufficient air is supplied.

Table 4 shows the simulated result for the overall

reduction of ZnO-ash with cokes, heated by LNG at heat loss of 2.94 kWh/h. Here, LNG is assumed to have 100wt% CH₄ for the simplicity.

The result can be summarized as follows: when 3.2 kg/h of ZnO-ash and 0.5 kg/h of cokes are mixed and are fed into a rotary kiln, 2.8 kg/h of Zn_g (see Table 4, product gas 25.21 kg/h \times Zn gas content 11.1 wt%) will form from the evaporation of metallic Zn and from the reduction of ZnO if heat is supplied by combustion of 1.2 kg/h of LNG with 20.4 kg/h of air. It also indicates that 0.02 kg/h of ZnO (see Table 4, product slag 0.09 kg/h \times ZnO content 26.62 wt%) will remain in slag as a solid.

As expected, this result is identical with that of Table 2. It is because both operations are thermodynamically same, except that the heat loss is considered for the simulation summarized in Table 4.

4. Pilot-plant Test

Based on the results from the simulation above, a process was engineered for the pilot-plant production of Zn_g from ZnO-ash in the rotary kiln at 1250°C at a rate of 3 tons/day. The evolved Zn_g was converted to ZnO with air in the oxidation chamber attached next to the rotary kiln. The produced ZnO powders were collected in the baghouse.

As shown in Fig. 4, the ZnO powders showed properties suitable to usual applications in ceramic industries with a purity of >95 wt% and an average particle size of ~3 μ m.

The overall Zn recovery from the ZnO-ash was about 85%. This number is somewhat lower than the numbers from the simulation and lab-scale test, which is not

Table 4. Simulated Result for the Overall Reduction of ZnO-ash with Cokes, Heated by LNG at Heat Loss of 2.94 kWh/h, T=1250°C, and P_{total}=1 atm

FEED	FLOW RATE (kg/h)		T (°C)									
ZnO-ash	3.20		25									
cokes	0.50		25									
LNG	1.20		25									
air	20.40		25									
PRODUCT												
gas	25.21		1250									
slag	0.09		1250									
ENERGY												
requirements are balanced with a rate of energy loss of 2.94 kWh/h.												
ANALYSES (wt%)												
FEED	C	CH ₄	CO	CO ₂	H ₂ O _g	N ₂	O ₂	SiO ₂	Zn _g	ZnO	Zn	
ZnO-ash	--	--	--	--	--	--	--	0.01	39.99	60	--	
cokes	88	--	--	--	--	--	--	12	--	--	--	
LNG	--	100	--	--	--	--	--	--	--	--	--	
PRODUCT												
gas (vol%)	--	--	3.85	9.07	15.15	64.77	--	--	4.96	--	--	
gas	--	--	3.69	13.66	9.34	62.06	--	--	11.10	--	--	
slag	--	--	--	--	--	--	--	68.39	--	26.62	5.0	

*Minor phases less than 3 wt% are deleted from the table.



Fig. 4. ZnO powders produced in the rotary kiln by the carbothermal reduction of ZnO-ash at 1250°C.

unusual in scale-up production. It is, however, expected that further refinements of the process can increase the Zn recovery above 90%.

The formation of ZnO powders itself by the carbothermal reduction is relatively simple compared to others such as the formation of SiC powders, SiC whiskers, Si₃N₄ powders, etc. It is, however, not the case in reality. For the later cases, the raw materials (silica and carbon) are usually available in a relatively pure form with the purity higher than 95%. In addition, the reactions are carried out in a well-controlled electric furnace with a flow of well-controlled gas mixture. Therefore, it is not very difficult to estimate the reactions in terms of thermodynamics.

For the formation of ZnO powders, however, the raw materials (either ZnO-containing ores or ZnO-containing wastes) are usually available in a complex mixture form with other ingredients. In addition, the energy for the reaction is usually supplied by the combustion of fuels such as coal, liquid natural gas, and liquid propane gas into a rotary kiln since the reaction temperature rarely exceeds above 1500°C.

Therefore, along with the formation of ZnO, various other reactions take place that make the routine thermodynamic consideration very difficult, if not impossible. This causes some critical problems on determining the optimum condition for the operation. Evidently, lower yield of ZnO as well as lower purity of the product can not be avoided.

In this regard, a powerful software such as PYROSIM is required to pinpoint the 'window' that can maximize the yield of ZnO. This study clearly demonstrated that the effectiveness of such approach by going through the simulation, the laboratory experiments, and the pilot-plant test.

IV. Conclusions

1. The production of ZnO powders from ZnO-ash via

the carbothermal reduction is realized by both the thermodynamic simulation and a lab-scale test.

2. Based on the results obtained from the thermodynamic simulation and a lab-scale test, a rotary kiln was built for the pilot-plant production of Zn₀ from ZnO-ash at 1250°C. The evolved Zn₀ was converted to ZnO powders with air in an oxidation chamber attached next to the rotary kiln. The produced ZnO particles showed properties suitable to usual applications in ceramic industries with a purity of >95 wt% and an average particle size of ~3 μm.

3. This study, which involves both the simulation and its experimental confirmation, will provide a valuable database and simulation format for the industries that treat Zn-containing waste. The differences in composition and operational condition of waste material do not pose any problem since some simple adjustments in input data are all needed to utilize these results.

Acknowledgement

This work was supported by MOST program "The Development of Mass Production Process for Fine ZnO Powders by Carbothermal Reduction (2N16370-32-1)."

References

1. J. G. Lee and I. B. Cutler, "Formation of Silicon Carbide from Rice Hulls," *J. Am. Ceram. Soc. Bull.*, **54**(2), 195-198 (1975).
2. J. G. Lee, R. Casarini and I. B. Cutler, "Sialon Derived from Clay to Provide an Economical Refractory Material," *Ind. Heating*, **XLIII**(4), 50-53 (1976).
3. J. G. Lee, P. D. Miller and I. B. Cutler, "Carbothermal Reduction of Silica," *Reactivity of Solid* (ed. by J. Wood *et al.*), Plenum Press, N.Y., 707-711 (1977).
4. J. G. Lee and I. B. Cutler, "Reactions in the SiO₂-C-N₂ System," *Nitrogen Ceramics* (ed. by F. L. Riley), Noordhoff Int. Pub., Netherlands, 175-181 (1977).
5. J. G. Lee and I. B. Cutler, "High-Performance Ceramics," *J. Korean Ceram. Soc.*, **14**, 33-49 (1977).
6. P. D. Miller, J. G. Lee and I. B. Cutler, "The Reduction of Silica with Carbon and Silicon Carbide," *J. Am. Ceram. Soc.*, **62**(3-4), 147-149 (1979).
7. J. G. Lee and I. B. Cutler, "Sinterable Sialon Powder by Reaction of Clay with Carbon and Nitrogen," *J. Am. Ceram. Soc. Bull.*, **58**(9), 869-871 (1979).
8. J. G. Lee, "산화물의 Carbothermal Reduction에 의한 고급 요업재료의 합성," *요업기술*, 224-225 (1979).
9. J. G. Lee, "Silica의 Carbothermal Reduction에 의한 질화 규소의 합성," *화학공공업의 진보*, **24**(11), 729-734 (1984).
10. H. J. Choi and J. G. Lee, "Continuous Synthesis of Silicon Carbide Whiskers," *J. Mat. Sci.*, **30**, 1982-1986 (1995).
11. B. Lightfoot, "Using Ausmelt Technology for Waste Treatment," pp. 975-87 in *Extraction and Processing for the Treatment and Minimization of Wastes*, Ed. by J. Hager *et al.*, The MMM Soc., 1993.

12. J. M. Floyd and W. E. Short, "Ausmelt Development of Top-submerged Lance Technology," Minerals Ind. Int., March, 18-24, 1994.
13. "Flame Reactor Technology: Applications Analysis Report," Horsehead Resource Development Co., EPA Report 540/A5-91/005, May, 1992.
14. A. F. S. Schoukens, G. M. Denton and R. T. Jones, "Pilot-plant Production of Prime Western Grade Zinc from Lead Blast-furnace Slags using the Enviroplas Process," pp. 857-68 in Proceedings of the Third International Symposium on Recycling of Metals and Engineered Materials, Ed. by P. B. Oueneau and R. D. Peterson, The MMM Soc., 1995.
15. N. A. Barcza, C. J. Hutton, M. J. Freeman and F. Shaw, "The Treatment of Metallurgical Wastes using The Enviroplas Process," pp. 941-62 in Extraction and Processing for the Treatment and Minimization of Wastes, Ed. by J. Hager *et al.*, The MMM Soc., 1993.
16. M. Matsuno, Y. Ojima and A. Kaikake, "Recent Development of EAF Dust Treatment Operation at Sumitomo Shisaka Works," pp. 432-41 in Zinc and Lead '95, Ed. by T. Azakami *et al.*, 1995.
17. N. E. Bottinelli, N. L. Kotraba and N. G. Bishop, "Method and Apparatus for Direct Reduction of Metal Oxides," U. S. Pat. No. 4 983 214, 1991.
18. F. H. Bricmont, "Furnace Dust Recovery Process," U. S. Pat. No. 4 673 431, 1987.
19. H. P. Discher, E. Greinacher and H. Banski, "Method and Installation for Removing Lead and Zinc from Foundry Dust," U. S. Pat. No. 5 547 490, 1996.
20. R. T. Jones, "PYROSIM, Steady-state Simulation of Pyrometallurgical Processes," Presented at Pyrometallurgy in the 90's, MINTEK, S. Africa, 1992.
21. T. Rosenqvist, Principles of Extractive Metallurgy, McGraw-Hill, Tokyo, 1974.
22. J. F. Keegel, "Methods for Recycling Electric Arc Furnace Dust," U. S. Pat. No. 5 538 532, 1996.
23. W. G. Bresser, M. Hirsch, A. Kaune and U. Harter, "Method of Reprocessing Metallurgical Residues, which Contain Zinc and Lead," U. S. Pat. No. 5 474 592, 1995.
24. N. Yamamoto, K. Takemoto, N. Sakamoto and Y. Iwata, "Method for Recovering Zinc from Zinc Containing Dust," U. S. Pat. No. 5 540 751, 1996.