T-1008

REDUCTION OF OXIDES WITH CARBON IN THE ELECTRIC-ARC FURNACE

By

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SUMMARY

This work covers a brief effort to determine the behavior of certain oxides at high temperatures in the presence of carbon. The oxides investigated were SiO_2, Al_2O_3, TiO_2, ZrO_2 and Fe_2O_3, with SiO_2 being of major interest. It is shown that the oxides of Si, Al, Ti and Zr react mainly in the gaseous state with carbon, and proceeds through the formation of a carbide. The oxides of Al and Fe showed appreciable reaction in the liquid phase as well as in the gaseous condition. The Fe reaction went to completion in a very short time.

An attempt is made to define the mechanism of the reduction of SiO_2. This is covered in some detail by experiments made in small graphite crucibles and laboratory-scale smelting trials. It is shown that as long as carbon is available, the gaseous oxide of silicon reacts with the carbon to form a carbide. This is shown in small graphite crucibles. No evidence could be found of crucible attack (liquid-solid reaction) or even crucible wetting by liquid SiO_2. In the laboratory-scale smelting trials designed to produce elemental silicon, in which the carbon is limited, it is shown that carbon, a carbide, and elemental silicon exist at the site of carbon particles. The silicon is attached to the carbide which is attached to the carbon. The evidence suggests strongly that the total reaction surface of the carbon is an important factor in the mechanism since the silicon is always nearest the heat source (electric arc). One would expect the rate of vaporization of the oxide of silicon to be important also.

It is further shown that the rate of the reduction reaction for producing elemental silicon may be increased by using finely divided materials. It would appear that in present commercial operations the reaction rate is controlled by the rather limited surface area since the carbon particles are large. With small particle sizes of carbon the rate could be controlled by the rate at which the oxide of silicon is vaporized. This implies that there may be an optimum particle size of carbon for which the rates are equal.

An increase in production rate is indicative only and further work should be carried out on a larger furnace. Several other operational advantages, however, would make the concept worthy of investigation.

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Organization	Material
Kaiser Refractories St. Louis, Missouri	Refractory
Great Lakes Carbon Corporation New York, New York	Electrodes
American Gilsonite Company Salt Lake City, Utah	Petroleum Coke
Tennessee Products & Chemical Corporation Nashville, Tennessee	Quartz and Coke

INTRODUCTION

The general problem dealt with in this investigation covers the reduction of metal oxides with carbon at high temperatures. The oxides of silicon, aluminum, titanium, zirconium, and iron are of interest. A macro-mechanism is presented for the reduction of silica with carbon and an analogy is drawn for alumina, titania, and zirconia. The experimental work is performed in a small-scale electric-arc furnace.

The element, silicon, has been of economic importance for many years. Commercial quantities of silicon, either as the element, or as in various alloys with iron called the ferrosilicons, are produced in electric-arc furnaces. The reduction of silica to silicon is accomplished with carbon and at extremely high temperatures attainable only in arc furnaces. In the main, elemental silicon is used by the aluminum industry and the various grades of the ferrosilicons are used by the steel industry. There are numerous other uses for silicon as well.

During World War II and for several years after, silicon was in high demand. Furnace capacity increased and the average size of furnaces increased greatly. When "normal" times arrived there was almost twice the furnace capacity that was required. In addition to this foreign competition increased. The result has been a drastic lowering of prices and increased operating costs due to idle equipment and other factors. The profit picture has suffered considerably and in some cases is non-existent.

In view of the above it would seem advisable to investigate some possible variations of existing practices in order to increase productivity. Unfortunately, the literature is very sketchy on practice although some information exists. A paper by Wise (1) is an example as applied to ferrosilicon containing 75 per cent silicon. It is known (2) that practices vary slightly from one producer to another in certain details. It can be said however, that silicon and the ferrosilicons are produced, in general, by the same techniques. There are adjustments made to allow for the iron content of the alloy being produced and for the level of the fixed carbon required in the smelting process. Large quartz, about 4 by 1 in., is mixed with predetermined quantities of reductant, usually 3 in. by down, and steel turnings which supply the iron. The reductants are coal, coke, and wood chips. The ash content of the reductants is kept as low as possible but runs, on the average, from 2 to 4 per cent, which places a limit on the purity of the product. It can be imagined that sampling a mixture of this sort just prior to smelting for final control would be extremely difficult and costly. This is not done and the operators depend on the accuracy of their batching system which includes the human element.

The high temperatures required for smelting are generated by the electric arc. Furnaces designed for smelting are operated with the heat source or arcs submerged and they are called submerged-arc furnaces. This means that the electrodes made of carbon or graphite, or conductors of the current, are made to arc under a cover of the mixture being smelted. The furnace therefore is full of mixture at all times and the electrode tips are buried, making the operation continuous. The mixture is added as it is required at the top and the product is withdrawn at regular intervals from the bottom at the hearth level. Successful practice depends on many factors, of which a homogeneous charge is one, and problems arise occasionally when segregation occurs in the mixture causing variations in resistivity. The furnace responds to such changes by raising or lowering the electrodes to allow for the change in resistivity and this generally requires local additions to the mixture to correct the condition. Control over the smelting operation requires close attention and considerable talent on the part of the operator. The product is handled in some fashion which need not be considered as essential to the work undertaken. It is to be noted that the recovery of silicon decreases as the silicon content of the alloy produced is increased. At the so-called silicon "metal" level recovery is about 65 per cent.

It may be seen from the brief description presented that certain short-comings are inherent in the process. These are listed as:

1) the level of impurities is high and under present practices there exists a limit to which they can be lowered prior to smelting.

2) the control of material blended for smelting is difficult and would be costly.

3) segregation occurs in the mixture being smelted that leads to operating difficulties which require the attention of an artist.

4) at higher levels of silicon the recovery is not good.

A scheme which would solve these problems as well as lend itself to all the grades of ferrosilicon on existing equipment could be the use of finely divided materials. Some industries use fine materials out of necessity, such as the non-ferrous people, and there have been considerable advances in the use of fines through some form of agglomeration. Vertman and Samarin (3) showed that the kinetics of their reaction was significantly improved by decreasing the particle size of the reactants. It may be possible to solve several problems with some changes and also cause an increase in the productivity. At any rate it would appear that work in this field should be done.

In order to gain an insight into the behavior of oxides at high temperature in the presence of carbon, several oxides should be investigated. It may be possible to classify oxides according to some general type of reaction. Although some elements of interest are not presently produced by carbon reduction it is believed that, with a better understanding of the behavior of their oxides, techniques will be developed to make this a reality. Any advance in this direction would certainly occupy the excess furnace capacity where applicable, and improve the overall economic and competitive picture.

The work of Vertman and Samarin (3) on effect of particle size on the reaction rate was carried out under a vacuum and it was noted that some vaporization occurred. Kroll and Schlechten (4) reported that considerable volatilization took place with oxides in a vacuum. Other problems in this work suggested that commercial applications using a vacuum were doubtful. Although vacuum technology is improving daily, its widespread use is still a long way off. At least as it applies to carbon reduction at high temperatures.

Vertman and Samarin report that a difference of opinion exists on the mechanism of reduction. One is that the diffusion of carbon is the rate-controlling step. The other, which is supported by Vertman and Samarin, indicates a surface type of reaction. Their work was done using chromic oxide and carbon. Regardless of the mechanism as seen today, it would appear that the use of finely divided reactants would enhance productivity. The splendid work done in the thermodynamic field on the identification and stabilities of various suboxides is extremely useful where it applies. References (5) through (9) are examples.

Unfortunately, for one reason or another, the information available is sadly lacking. Research and development is the answer and it is hoped that some interest can be stimulated and that in the future significant contributions will be made in this area.

EQUIPMENT AND MATERIALS

The furnace used in this work is shown in Fig. 1. Power is supplied by two welding generators which will deliver up to 24 kw d.c. Any desired load may be selected at the generators and a constant load is delivered, that is, the product of voltage and amperage is constant. The current is applied through the electrode with positive polarity and is returned through a graphite bottom with negative polarity. This arrangement is necessary in order to prevent the formation of a cavity on the bottom (or hearth). There is no regulator on this furnace and the desired relationship between voltage and amperage is maintained manually by raising or lowering the electrode thereby adjusting the gap through which the arc must travel (resistance). Most arc furnaces, industrial or otherwise, operate on a.c. power and it is not known whether or not using a.c. or d.c. would affect the results. The writer feels it would make no difference since all furnaces are heaters only.

All materials used in this work were of the chemically pure variety with the exception of the quartz, reductant, and the electrode stock.

Fig. 1. Arc Furnace Used in the Experimental Work.

The quartz is mined in North Carolina and is available and used in industrial quantities. The analysis is as follows:

Constituent	Per cent
SiO_2	99.50
Al_2O_3	0.15
Fe_2O_3	0.05
CaO + MgO	0.05
Other	Balance

It was decided to use this material since it is the purest variety from which the desired particle sizes could be obtained.

The petroleum coke used as the reductant was calcined and contained the following:

Constituent	Per cent
Fixed Carbon	98.00
Ash	0.69
VCM	Balance

Petroleum coke is used industrially in small amounts and is not calcined in which case the VCM is considerably higher and the fixed carbon proportionally lower.

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental effort is divided into three parts, each of which will be treated separately. The first part deals with the preliminary work on various oxides to determine their early behavior in the presence of carbon at high temperatures. The second part is a continuation of the first covering the behavior of SiO_2 in an attempt to determine the mechanism of reduction of SiO_2 to Si. The third is an attempt to study the effect of particle size on the reduction rate of SiO_2.

Preliminary Studies

Small graphite crucibles were prepared from furnace-electrode stock. They were 1½ inches in diameter and 1½ inches high. A hole was drilled 5/8-inch diameter to within ½-inch of the bottom. The cavity was packed with oxide and the crucible was buried in a bed of petroleum coke 4 x 6 mesh. It was found by trial and error that one inch of coke on the bottom with 1½ inches over the top gave the desired results. The current was passed through the mass and extremely high temperatures were generated by the arcing between the particles of coke. This provided a sufficiently high temperature in a relatively short time. It is believed that the temperature was in the neighborhood of 2500°C. The general arrangement used is shown in Fig. 2. A current of 300 amperes at 45 volts was used for various periods of time. Actual arc temperature is believed to be about 3500°C.

The oxides of silicon, aluminum, titanium, zirconium, and iron were treated in the manner outlined at various times. Fig. 3 shows the results of this treatment and the times are total. X-ray diffraction techniques (powder patterns) were employed to identify the compounds at the top and bottom of each crucible. Table 1 gives the summary of this work.

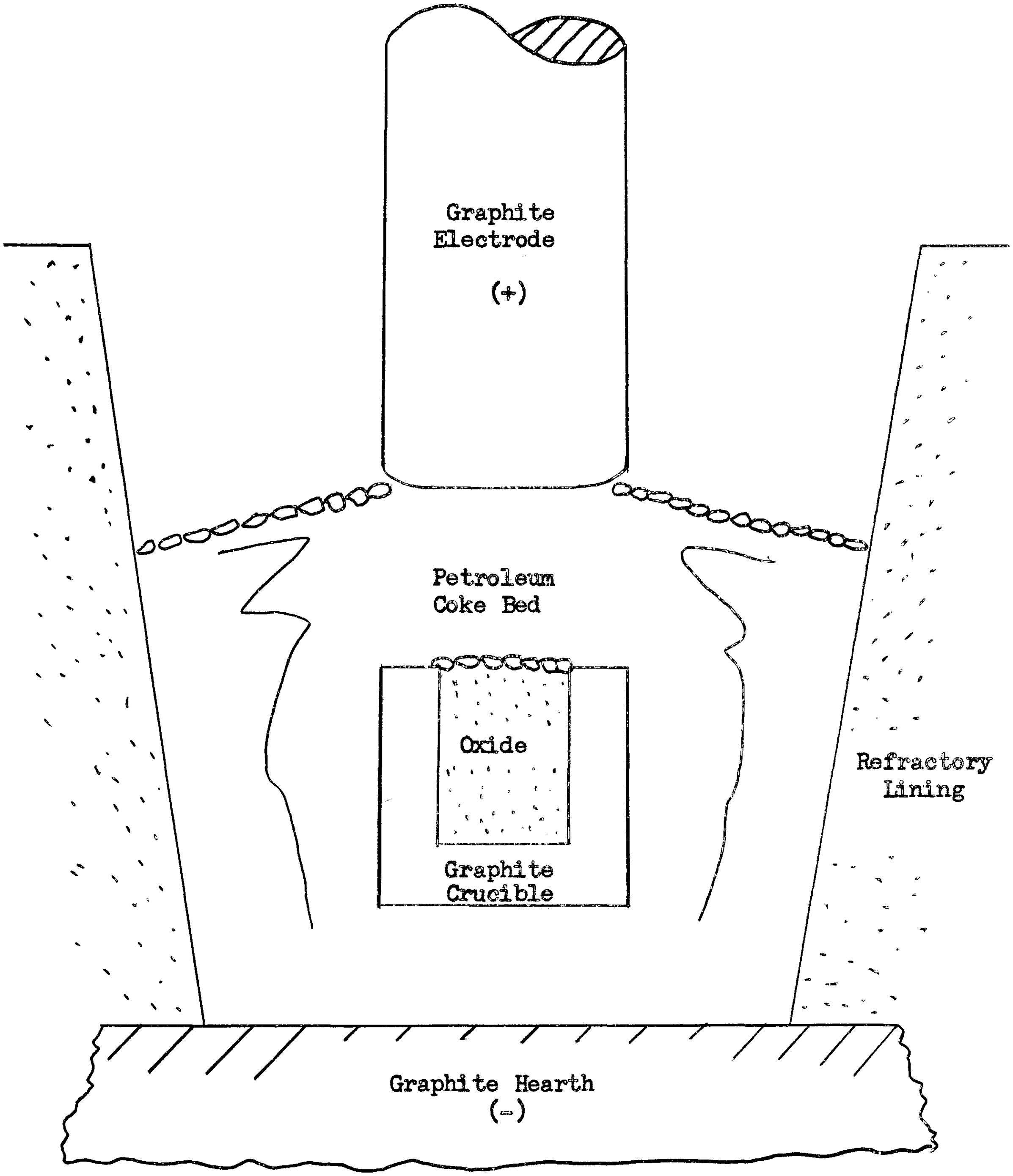
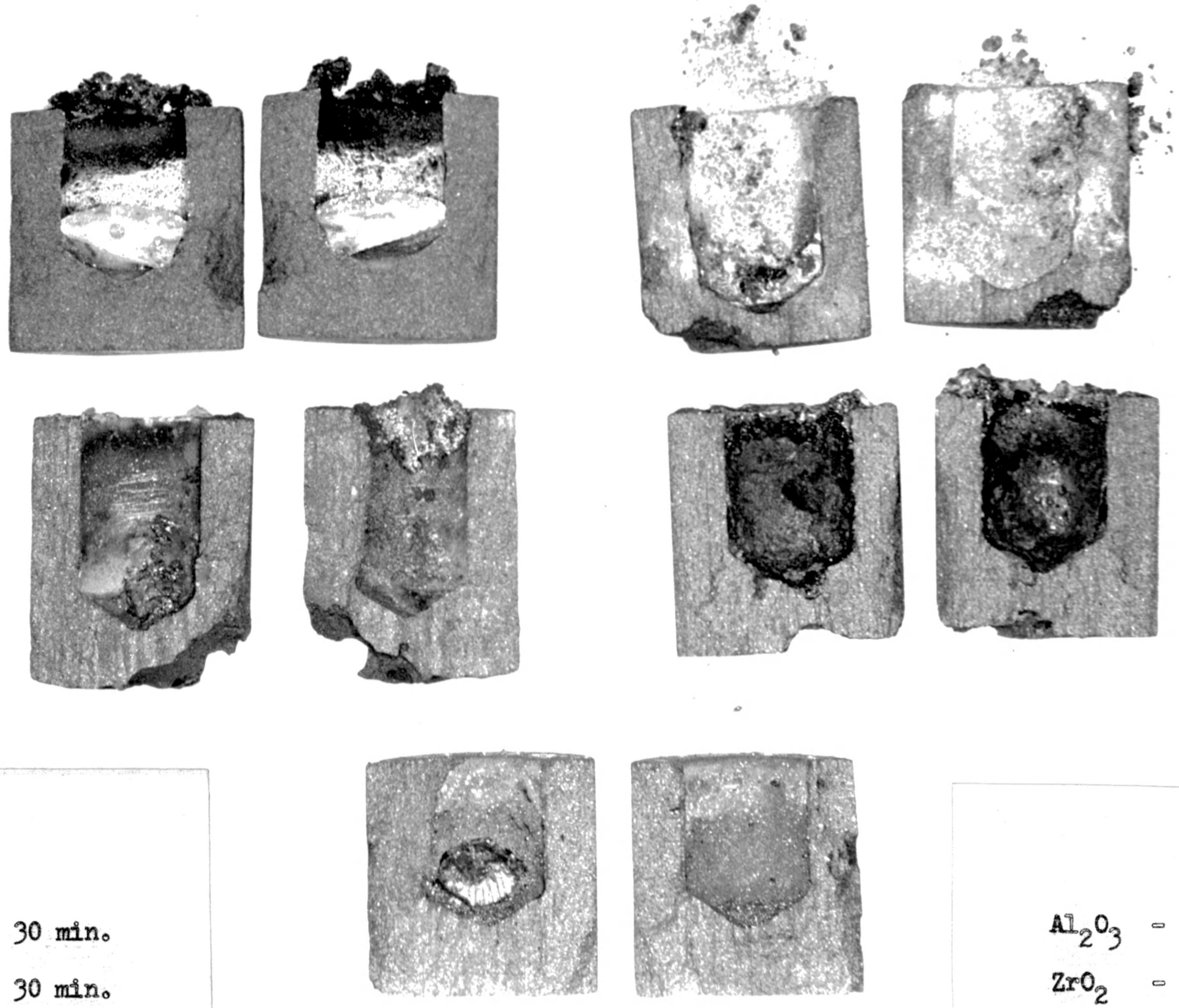


Fig. 2. Arrangement for the Study of Behavior of Oxides in Presence of Carbon at High Temperatures.



SiO_2 - 30 min.

TiO_2 - 30 min.

Al_2O_3 - 30 min.

ZrO_2 - 30 min.

Fe_2O_3 - 5 min.

Fig. 3. Specimens After Heating for Various Times.

Table 1. Identification of Compounds at Top and Bottom of Crucible After Heating of Oxide.

Oxide	Position	Compound Identified
SiO_2	Top	α-SiC
	Bottom	No Pattern - Fused Quartz
Al_2O_3	Top	Al_4C_3
	Bottom	Al_4C_3
TiO_2	Top	TiC
	Bottom	TiO_2
ZrO_2	Top	ZrC
	Bottom	ZrO_2
Fe_2O_3	Top	Fe
	Bottom	Fe

Behavior of SiO_2

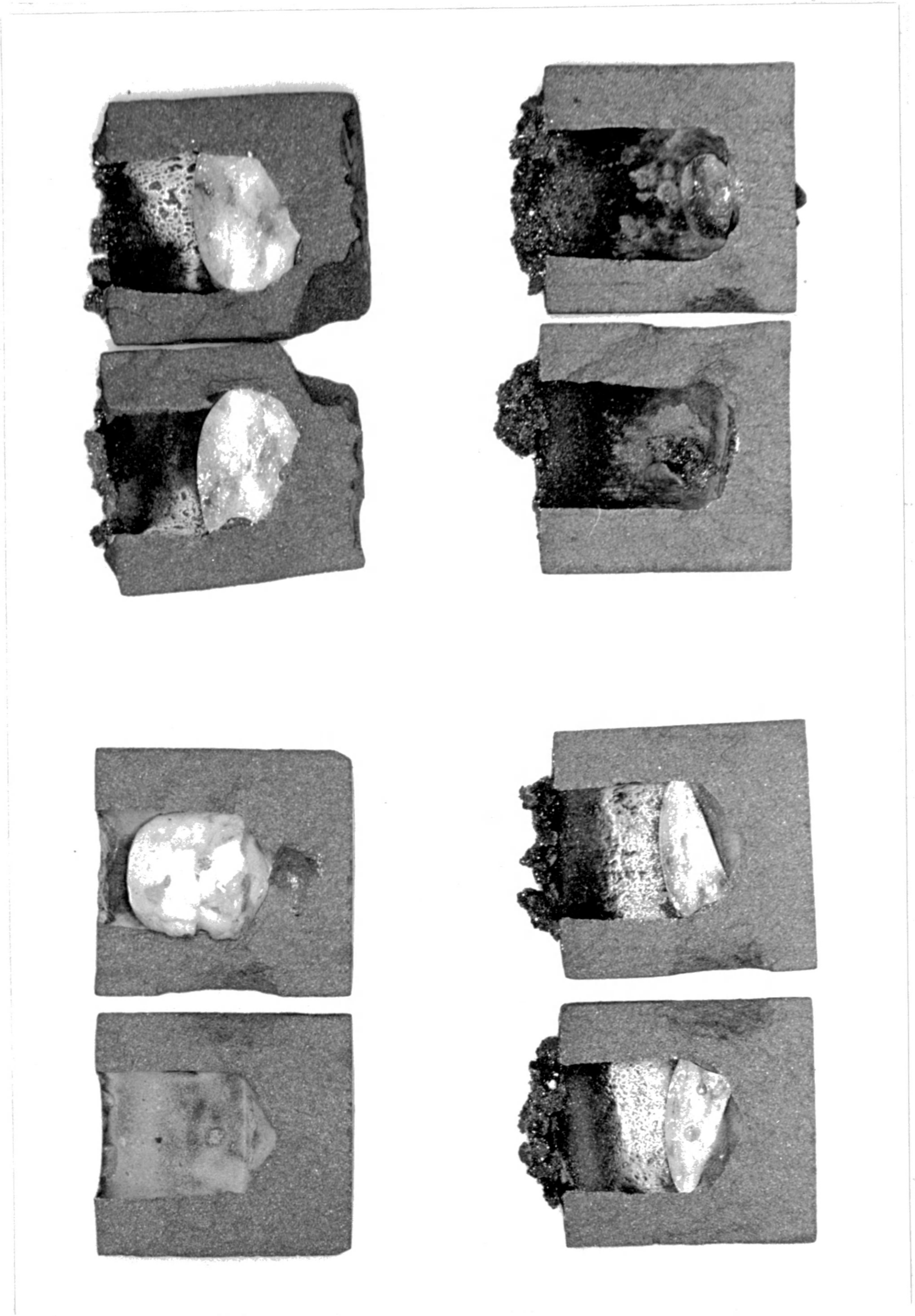
The same scheme given in the preceeding section was used and a continuation of this type of study was made on SiO_2. Silica was heated for varying times to determine if any changes occurred in the product with time. Fig. 4 shows the results of heating for the times indicated. There can be seen no evidence of crucible attack (or even wetting). Fig. 5 shows the same thing continued for 3½ hours of heating. In this case the crucible was removed from the furnace after each hour and the SiO_2 replenished. It was necessary to cut off the top of the crucible after each withdrawal in order to salvage the compound formed at the top and after the second hour a new crucible had to be used.

Fig. 6 shows the results of heating different combinations of materials in the graphite crucibles. All times are again total. The silicon was a commercial variety and was powdered. The SiC was also an industrial material and the SiO_2 used was high purity α-quartz. These were mixed but not compacted. The combination of SiO_2 + C was in the form of pellets as used in the smelting trials.

Table 2 gives the summary of all the work in this study.

Table 2. Summary of Work on SiO_2 and Other Materials.

Material	Time, Min.	Compound Identified
SiO_2	5	Increasing amounts of α-SiC at top
"	15	
"	30	
"	60	
"	210	
Si	30	α-SiC
$SiC + SiO_2$	30	α-SiC
$SiO_2 + C$	30	α-SiC



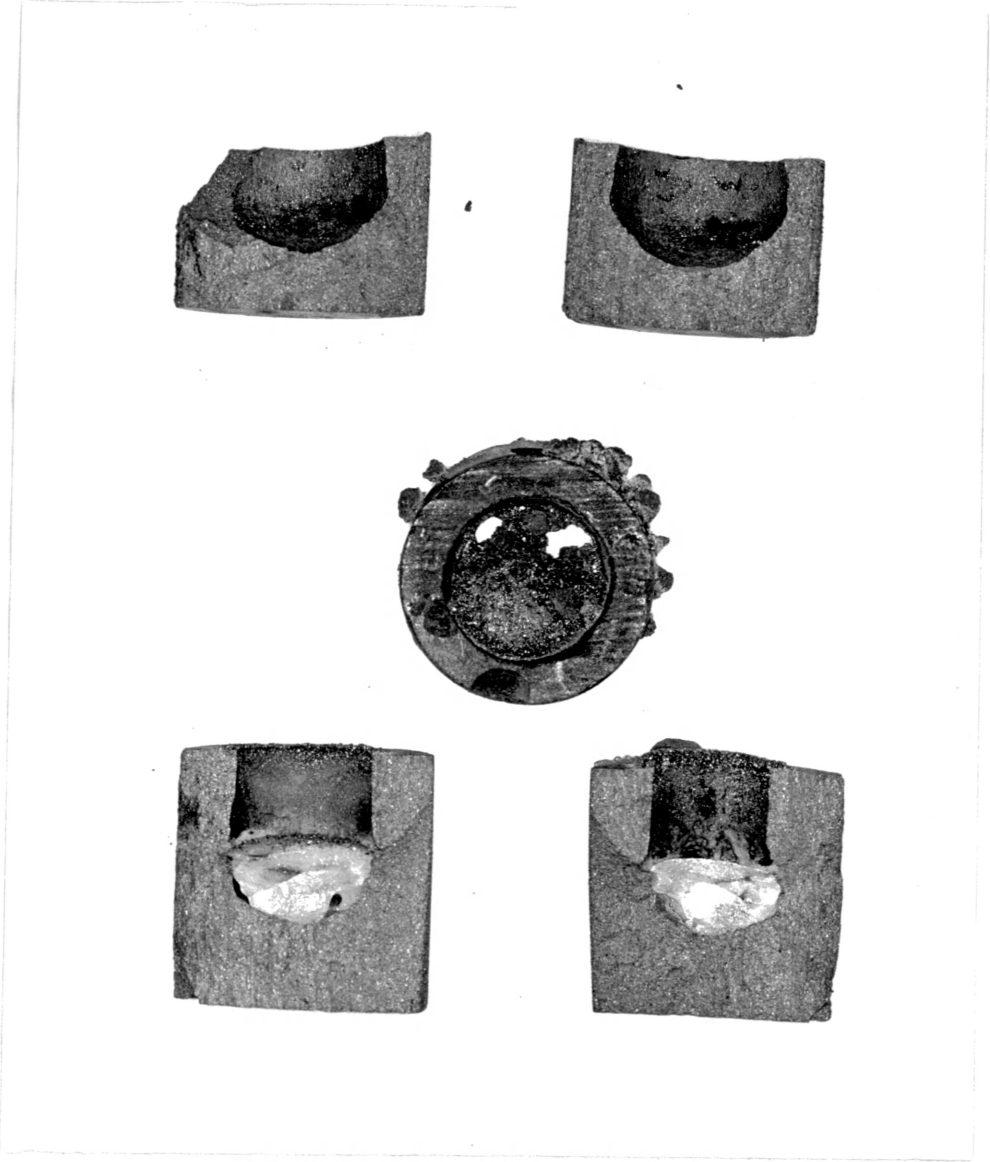
5 min.

30 min.

15 min.

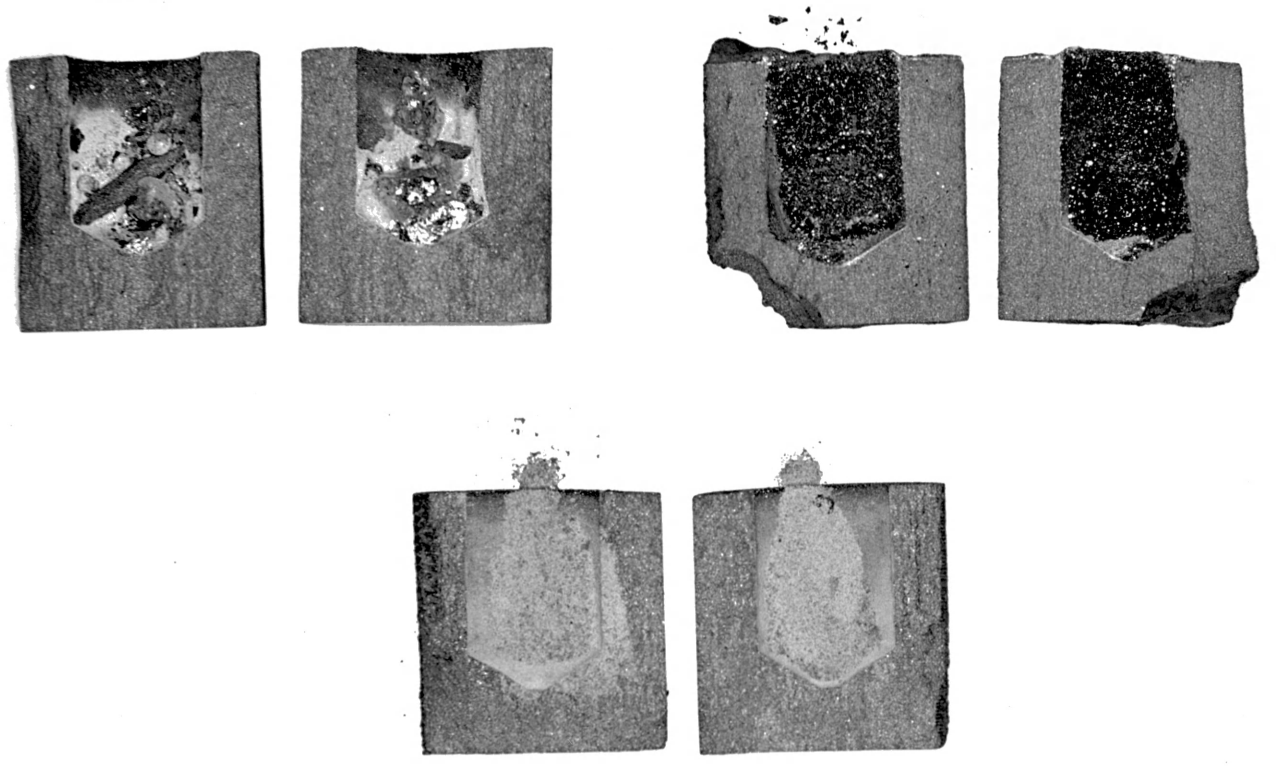
60 min.

Fig. 4. SiO_2 Heated for Various Times.



210 min.

Fig. 5. Continuation of Heating SiO_2 as in Fig. 4.



Si - 30 min

$SiC + SiO_2$ - 30 min.

$SiO_2 + C$ - 30 min.

Fig. 6. Various Materials Heated for Time Shown.

Effect of Particle Size on the Reduction Rate of SiO_2

Duplicate heats were made using carefully sized silica and calcined petroleum coke. The sizes investigated were 4 x 6 mesh, 8 x 10 mesh, and minus 100 mesh. The reactants were used in stoichiometric proportions to yield silicon and they were well mixed. The minus 100 mesh blend was pelletized using sugar as a binder, and dried prior to smelting. The reaction of interest is:

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

A complete log of each heat is included in the Appendix, together with the appropriate weights and measures.

The procedure used in making these heats was developed by the writer after several years experience on furnaces of all sizes. It amounts to arcing on a coke bed for a period of time called the pre-heat. The coke bed is used to prevent the oxidation of the graphite hearth. After preheating the charging of the reactants is started. This is done rather slowly and around the sidewalls of the furnace crucible. The level of the mixture is raised slowly enough to allow sufficient time for the formation of the inner crucible, which is the smelting zone. Once the crucible is formed and the arc is submerged the level of the mixture may be raised at a slightly higher rate. It can be seen that the mixture of reactants makes its own lining. The mixture is then added as required after adequate stoking which means pushing the mixture toward the bottom of the inner crucible manually from the top. The gaseous reaction products rise to the surface of the mixture the combustible portion of which ignites.

Fig. 7 shows a sketch of the furnace in operation.

Table 3 gives the pertinent data for the six heats on the effect of particle size on reduction rate.

Figs. 8, 9 and 10 show the relative size of particles used in these heats and a section of the crucible from one heat in each set. The crucibles were essentially spherical in shape except at the bottom where the product collects (see Fig. 7).

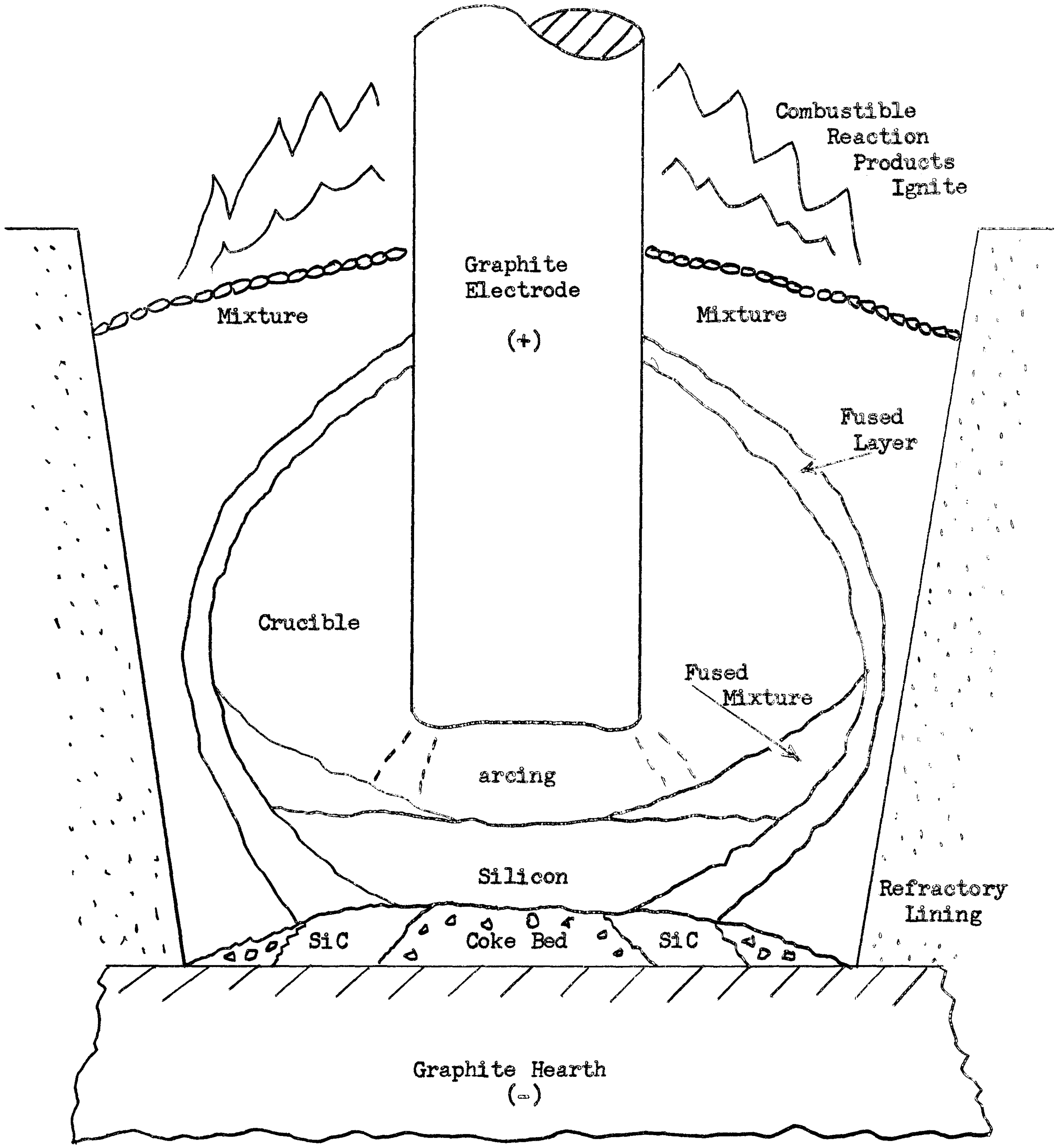


Fig. 7. Arrangement for Smelting Studies.

Table 3. Pertinent Data from Smelting Trials.

Heat	Particle Mesh Size	Condition of Reactants	Time, minutes			Weight Grams Silicon	g Si/min. Smelt
			Preheat	Crucible	Smelt		
1	4 x 6	Loose and mixed	30	20	137	243	1.77
1a			30	20	117	288	2.46
2	8 x 10	Loose and mixed	30	20	125	512	4.09
2a			30	20	135	560	4.15
3	minus 100	Blended and pelletized	30	20	87	358	4.12
3a			30	20	140	669	4.77

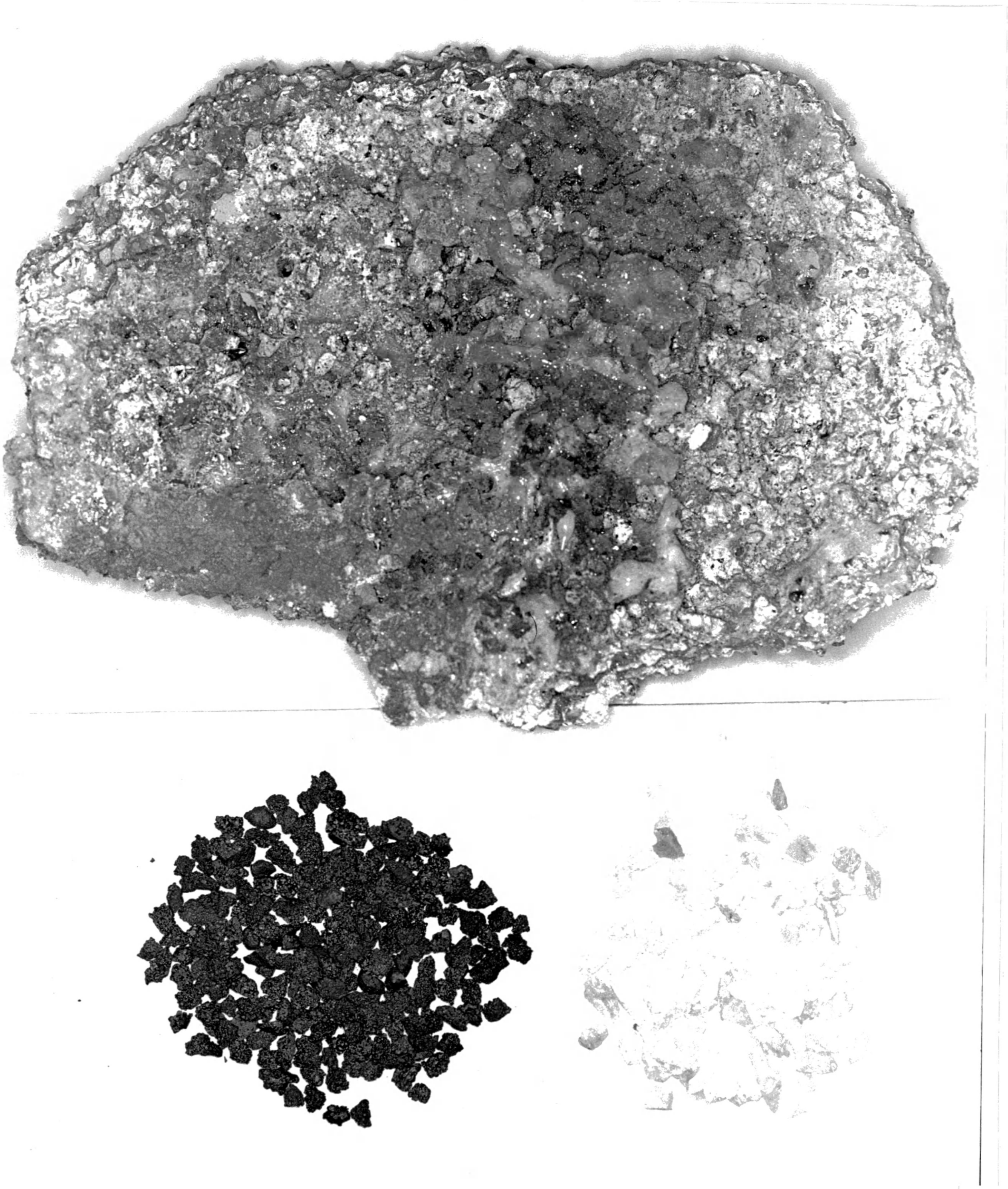


Fig. 8. Particle Sizes and Section of Crucible Representing Heats 1 and 1a.

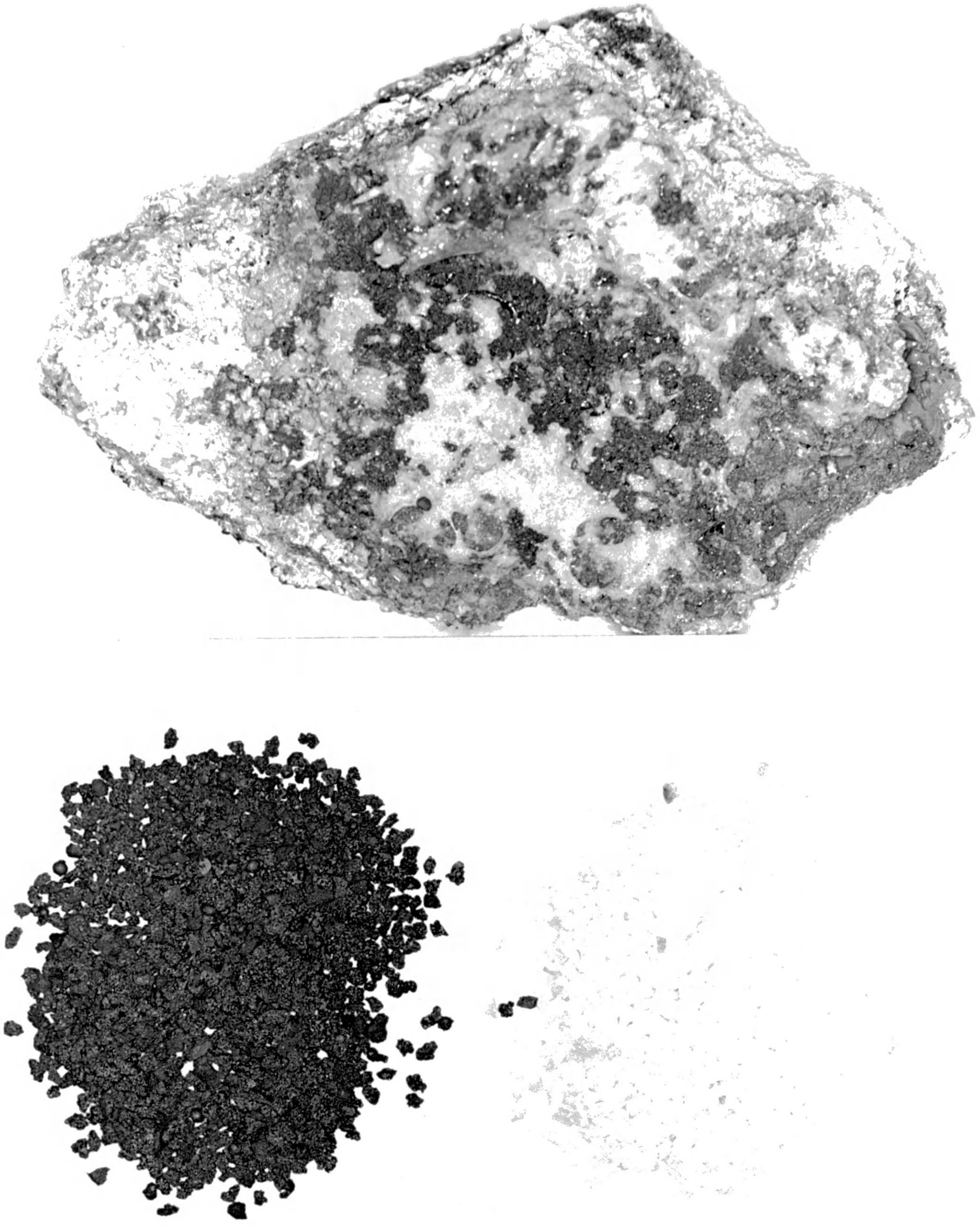


Fig. 9. Particle Sizes and Section of Crucible Representing Heats 2 and 2a.

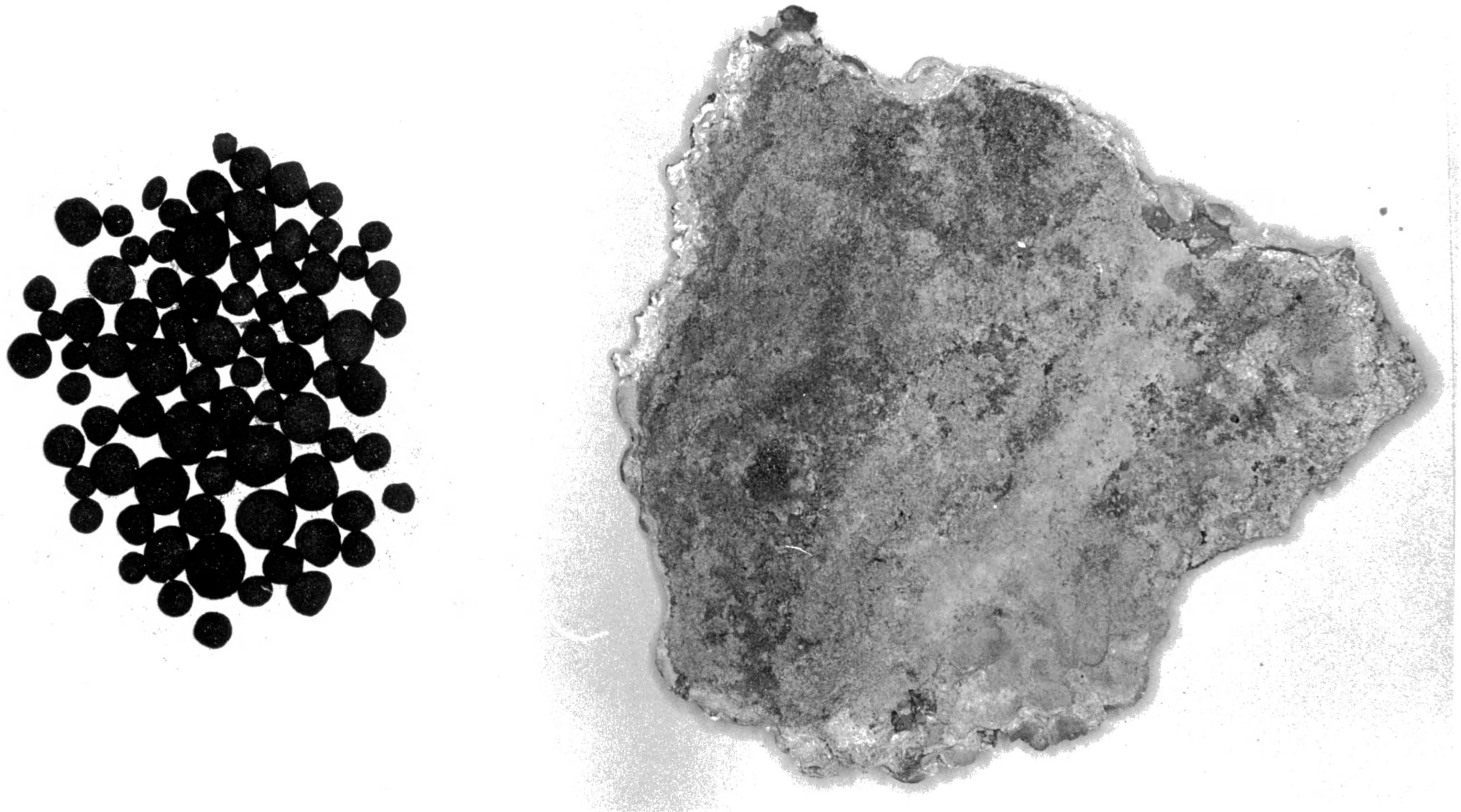


Fig. 10. Pelletized Mixture and Section of Crucible Representing Heats 3 and 3a.

DISCUSSION

An effort is made to discuss each part of this work separately even though some overlap is unavoidable. It is essential, for example, to use information gained in one part of the investigation to explain a point in another.

Preliminary Studies

This part of the work covers a preliminary study on the early behavior of the oxides of silicon, aluminum, titanium, zirconium, and iron. It is shown that iron reacts with carbon at high temperatures and that the reaction goes to completion in a short time. It may be said that the iron was used as a control. The reaction is certainly well known and needs no comment here.

Silica, alumina, titania, and zirconia react with carbon at high temperatures to form carbides. These are identified as α-SiC, Al_4C_3, TiC, and ZrC. The carbide of aluminum reacts with water to form the hydroxide and methane.

The carbides exist as long as carbon is present. This was shown to be true for silicon carbide and one would expect, by analogy, that the same holds true for the other carbides as well. This also occurs when a reaction first begins even in a system which is stoichiometrically balanced to provide the element because of a localized abundance of carbon. One would expect that carbon diffusion is involved but the vapor pressure of the carbon at high temperatures is not to be disregarded. The carbide forms at first which then reacts with the additional oxide in the system to yield the element.

It is known that silicon is produced commercially according to the following equation:

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

The level of the fixed carbon used in practice ranges from 93 to 97 per cent of the theoretical amount required. The carbon contributed by the electrodes is not generally considered. If an excess of carbon is used silicon carbide is formed. If three moles of carbon are used per mole of SiO_2 all carbide will result.

The following overall reactions are given to show that an analogy is possible for the oxides in question:

$$SiO_2 + 2C \longrightarrow Si + 2CO \qquad (1)$$

$$\underline{SiO_2 + 3C \longrightarrow SiC + 2CO} \qquad (2)$$

$$\begin{array}{llllllll}
Al_2O_3 & + & 3C & \longrightarrow & 2Al & + & 3CO & (3) \\
2Al_2O_3 & + & 9C & \longrightarrow & Al_4C_3 & + & 6CO & (4) \\
\hline
TiO_2 & + & 2C & \longrightarrow & Ti & + & 2CO & (5) \\
TiO_2 & + & 3C & \longrightarrow & TiC & + & 2CO & (6) \\
\hline
ZrO_2 & + & 2C & \longrightarrow & Zr & + & 2CO & (7) \\
ZrO_2 & + & 3C & \longrightarrow & ZrC & + & 3CO & (8) \\
\hline
\end{array}$$

Since it is known that Eq. (1) is used commercially it is not unlikely that Eqs. (3), (5), and (7) would yield the element as well. Details of the operation would vary according to the nature of the products. The level of impurities is not considered here and the product would no doubt require refining. Desirable combinations of the oxides are also to be considered.

Linear standard free energy charts show that the only difference would be in the operating temperatures required. These temperatures are readily obtainable in the electric-arc furnace and are as follows:

Oxide	Temperature, °C
SiO_2	1550
Al_2O_3	2010
TiO_2	1650
ZrO_2	2170

The above temperatures are for Eq. (1), (3), (5), and (7) from which the element is produced and represent the temperature at which carbon monoxide has a larger negative free energy of formation than the oxide (ΔG^{o} for the reaction is zero).

It should be pointed out that the behavior of these oxides dictates that at the temperatures involved even a partial vacuum should be avoided. Investigators have reported that the use of vacuum techniques, even at lower temperatures, has led to problems with volatilization. It would be possible, however, to produce metals from oxides which do not vaporize at reaction temperatures in a vacuum.

Behavior of SiO_2

It can be seen from the results of using various combinations of materials that silicon carbide is the predominant product when carbon is present in abundance. The work on laboratory-scale smelting trials, covered in the next section, shows that carbon, silicon carbide, and silicon exist separately and that the carbon surface is occupied. It may be said then that the first step of the reaction is the volatilization of SiO_2 as $SiO + \frac{1}{2}O_2$. The oxygen reacts with carbon to form CO at high temperatures. The SiO reacts with carbon to form SiC and CO. SiC then reacts with additional SiO to form Si and CO.

From the above, the following mechanism for the reduction of SiO_2 with carbon at high temperatures is suggested:

$$\begin{array}{lllll}
2SiO_{2(l)} & \longrightarrow & \cancel{2SiO}_{(g)} & + & \cancel{O}_{2(g)} \\
\cancel{SiO}_{(g)} + 2C_{(s)} & \longrightarrow & \cancel{SiC}_{(s)} & + & CO_{(g)} \\
2C_{(s)} + \cancel{O}_{2(g)} & \longrightarrow & 2CO_{(g)} & & \\
\cancel{SiC}_{(s)} + \cancel{SiO}_{(g)} & \longrightarrow & 2Si_{(l)} & + & CO_{(g)} \\
\hline
2SiO_{2(l)} + 4C_{(s)} & \longrightarrow & 2Si_{(l)} & + & 4CO_{(g)}
\end{array}$$

The above mechanism suggests that the silicon is formed at the surface of the carbon which was previously converted to silicon carbide. This condition was observed in the smelting trials.

The formation of the carbide must take place rapidly since carbon monoxide is the more stable. The formation of carbon monoxide in the reaction between carbon and oxygen must take place instantaneously. The final reaction must require most of the energy suggesting that the reaction would depend on the number of active carbon surfaces available and not carbon diffusion. One cannot imagine that a gas-solid reaction of this type depends on carbon diffusion since there is an intermediate product. In a commercial operation this would explain the low recovery of silicon, and, why the use of finely divided material, with more surface area, would increase the reduction rate. Further, at the temperature involved the vapor pressure of the carbon is significant, and it may be possible that SiO and carbon react to some extent when both are in the gaseous state. It is known that, in commercial furnaces, SiC forms around the electrodes on top of the mixture, where temperatures are low, when too much carbon is present. Silicon carbide also forms in the smelting zone. In the vernacular, this situation is referred to as an "over-coked" condition.

Published thermodynamic data show that SiO is stable above 2100°K. Volatility data (10,11) only indicate that the main reaction involved in vaporization of SiO_2 at high temperatures in a vacuum is:

$$SiO_{2(s)} = SiO_{(g)} + \tfrac{1}{2}O_{2(g)} \qquad (1)$$

The total vapor pressure over $SiO_{2(s)}$ at 1600°C has been reported as 4.38×10^{-6} atmosphere. The standard free energy change for the above reaction at 1600°C can be calculated as follows:

$$P_T = p_{SiO} + p_{O_2} = 4.38 \times 10^{-6} \text{ atm}$$

$$p_{O_2} = \tfrac{1}{2}p_{SiO}$$

$$\therefore \quad p_{SiO} = 2.92 \times 10^{-6} \text{ atm}$$

$$\text{and} \quad p_{O_2} = 1.46 \times 10^{-6} \text{ atm}$$

$$K = \left[p_{SiO}\right]\left[p_{O_2}\right]^{\frac{1}{2}} = 3.54 \times 10^{-9}$$

$$\therefore \Delta G^{o} = -4.58(1873)\log 10^{-8.45}$$

$$\Delta G^{o} = +72,600 \text{ cal}$$

With additional information it is interesting to show the effect of the presence of carbon on the partial pressure of $SiO_{(g)}$. Consider the reaction

$$C_{(s)} + \tfrac{1}{2}O_{2(g)} = CO_{(g)} \qquad (2)$$

$$\text{for which } K_{1600^{o}C} = 10^{7.68}$$

If the sum of reactions (1) and (2) is considered, then:

$$SiO_{2(s)} = SiO_{(g)} + \tfrac{1}{2}O_{2(g)} \quad (K = 10^{-8.45})$$

$$\underline{C_{(s)} + \tfrac{1}{2}O_{2(g)} = CO_{(g)} \quad (K = 10^{7.68})}$$

$$SiO_{2(s)} + C_{(s)} = SiO_{(g)} + CO_{(g)} \quad (K = 10^{-0.77})$$

$$(p_{SiO})(p_{CO}) = 10^{-0.77}$$

Since P(total) $= p_{CO} + p_{SiO} + p_{O_2} + p_{CO_2}$ and

$p_{O_2} + p_{CO_2}$ are negligible

therefore $p_{SiO} = p_{CO}$

and $p_{SiO} = 10^{-0.385} = 0.41$ atm

Even though the data may be in error, and reference is made to 1600°C, the effect of carbon on the vapor pressure of $SiO_{(g)}$ is quite pronounced, i.e., 2.92×10^{-6} atm in the absence of carbon and 0.41 atm in the presence of carbon. One would expect a more remarkable increase at arc temperatures

Effect of Particle Size on the Reduction Rate of SiO_2

The laboratory-scale smelting trials were made with the conditions controlled as closely as possible. It must be mentioned, however, that the nature of the work leads to semi-quantitative results and that these data are indicative only. The reasons are that 1) continuous operation of a small furnace for a sufficiently long period to provide enough product for handling is extremely difficult if not impossible, 2) the bulk of the charge in the furnace is in various stages of reduction so that suitable collection of the product is impossible, and 3) an analytical procedure for determining the amounts of the various compounds is not known.

Fig. 11 shows the reduction rate as a function of the particle size of the reactants. Both the silica and reductant were sized identically although it would seem the quartz sizing would not be too critical since fusion and vaporization take place. The silica must be sized for convenience, however, particularly when agglomeration is required. Since the curve is not strictly quantitative no effort is made to evaluate this further. A significant increase in reduction rate is indicated and additional work should be done on a larger scale. It is felt that the improvement is due to the increase in surface area of the carbon available for reaction.

The use of finely divided materials, particularly a size suitable for agglomeration, offers certain advantages over present practices and these are enumerated as follows:

(1) a grade of reductant can be used in which the ash content (impurity level) is low thereby providing a product of higher purity.

(2) only one reductant is required rather than 3 or 4.

(3) close chemical control may be exercised just prior to smelting.

(4) the technique lends itself to automation.

(5) a homogeneous furnace feed would result giving improved operating stability.

(6) recovery of silicon should be improved.

(7) the scheme would apply to all of the ferrosilicons and to alloys other than ferrosilicon.

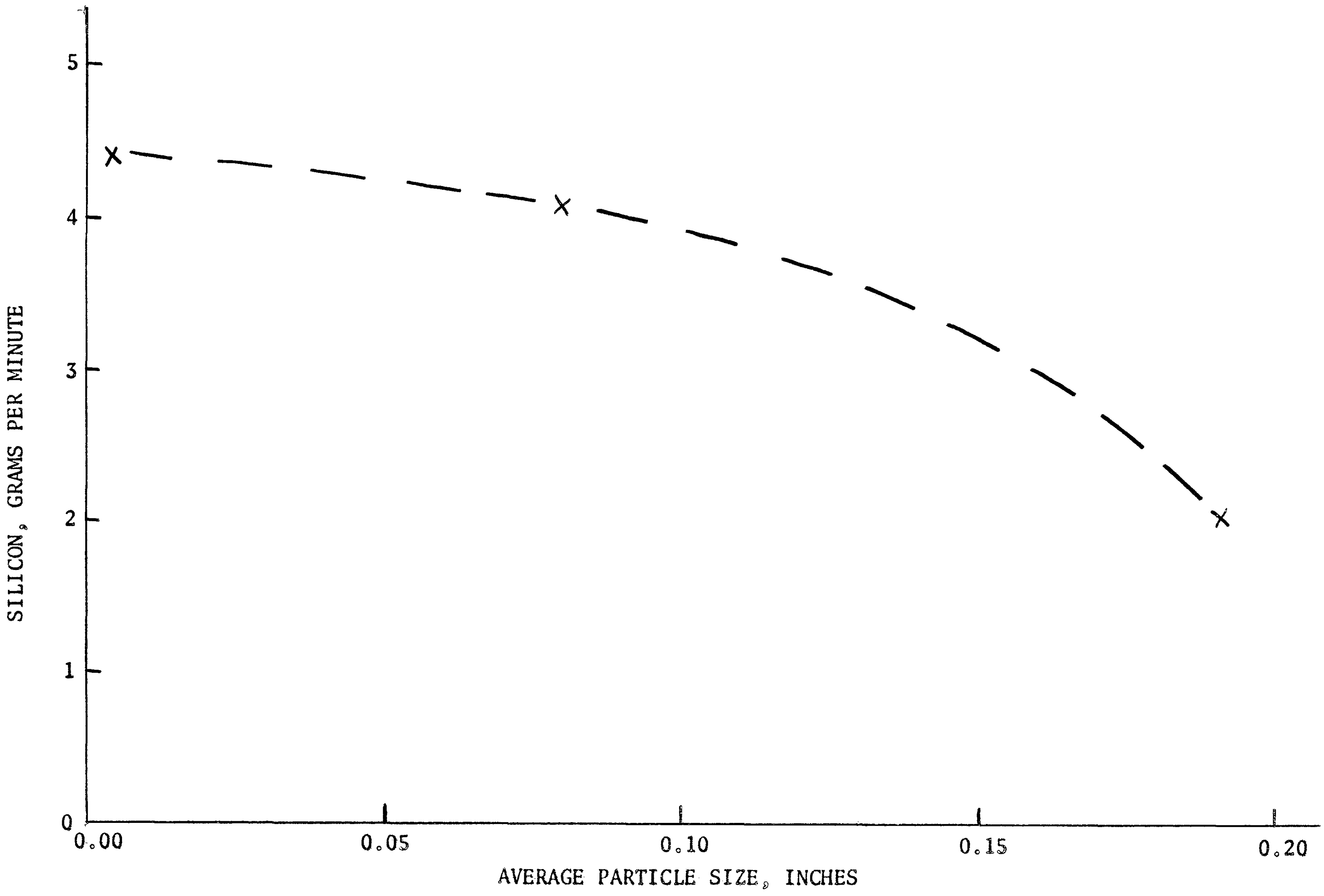


Fig. 11. Reduction Rate as a Function of Average Particle Size.

CONCLUSIONS

Although the work covered is preliminary in nature and introduces an area of study in which considerable work needs to be done, the following conclusions are drawn:

1) Silica, alumina, titania and zirconia are vaporized at high temperatures and react with carbon to form a carbide.
2) Silicon carbide reacts further with additional oxide of silicon, probably a suboxide, and elemental silicon is produced.
3) The reduction of silica is a gas-solid reaction, the rate of which depends on the surface area of the carbon available.
4) Decreasing the particle size of both reactants shows a significant increase in reaction rate.

Additional studies are required to learn more about the behavior of the oxides mentioned as well as others. Efforts should be made on the feasibility of producing aluminum, titanium, and zirconium directly by carbon reduction. Further study should be made on the effect of particle size on reaction rates and would best be accomplished on a furnace of intermediate size of at least 500 kva.

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Appendix

RECORD OF HEAT NO. 1

Date: 12/7/63

Materials: Coke 4 x 6 mesh (98% F.C.)

Gravel 4 x 6 mesh (99% SiO_2)

Mixture Order: Coke 2448 g

Gravel 6036 g

100% carbon theory

Preparation: Rolled in drum. Dumped on floor and mixed just prior to charging.

Charging: By hand as required. Stoking as required.

Weights: Coke bed 300 g (4 x 6 mesh)

Electrode	-	Start	1260 g
		End	1048 g
		Used	212 g

Performance: See following log.

Performance:

Time	Volts	Amperes[(a)] Reading	Actual	KW	Remarks
10:25	50	130	270	13.50	Start preheat. 200 N generator Setting[(b)]. Arcing on coke bed.
10:30	65	100	150	9.78	
10:35	49	190	285	13.95	
10:40	55	150	225	12.38	
10:45	61	110	165	10.07	
10:50	50	180	270	13.50	
10:55	55	150	225	12.38	Start charging slowly around sidewalls to form crucible. Load picked up and steady. Preheat 30 min.
11:00	35	230	345	12.08	Load steady.
11:05	35	240	360	12.60	Crucible forming. Charged at end of period.
11:10	40	220	330	13.20	Crucible continuing to form. Arc almost completely covered.
11:15	43	200	300	12.90	Crucible O.K. Arc covered. Load is steady. Crucible formation 20 min.
11:20	42	210	315	13.23	Continue with charging as required. Heavy blue flame over mixture.
11:25	40	215	322	12.90	Load steady. Crucible getting wider. Gas flame at tap hole.
11:35	40	210	315	12.60	Load Steady. Top stoked in. Crucible O.K. Good flame pattern.
11:45	45	190	285	12.83	Load steady. Stoked and covered.
11:50	47	180	270	12.70	Stoked in and covered.
12:00	48	180	270	12.96	Load steady.
12:10	48	180	270	12.96	
12:20	47	190	285	13.40	Stoked in and covered. Big crucible.
12:25	41	210	315	12.90	
12:35	47	180	270	12.70	
12:45	46	190	285	13.10	Stoked and charged as required.
12:50	50	170	255	12.75	
1:00	45	190	285	12.83	
1:15	45	200	300	13.50	All mixture in furnace.
1:30	46	190	285	13.10	
1:32	45	200	300	13.50	Electrode freed. Power off. Metallic specks on electrode top. Smelting time 137 min.

(a) Ampere factor x 1.5 because of shunt.
(b) Same for all heats.

Result: Had large crucible. More stoking would close it in some. Metal well collected at electrode tip with silicon carbide below metal. Some metallic specks on wall of crucible.

Unreacted mixture	3988 g
Partially reacted and fused	2345 g
Metal - SiC - C	405 g
60 - 30 - 10	243 g
Metal	243 g

Comments: Figures for power consumption and electrode consumption not determined.

RECORD OF HEAT NO. 1a

Date: 12/8/63

Materials: Coke 4 x 6 mesh (98% F.C.)

Gravel 4 x 6 mesh (99.5% SiO_2)

Mixture Order: Coke - 2448 g

Gravel - 6036 g

100% carbon theory

Preparation: Rolled in drum. Dumped on floor and mixed just prior to charging.

Charging: By hand as required. Stoking as required.

Weights: Coke bed 300 g (4 x 6 mesh)

Electrode -	Start	1048 g
	End	806 g
	Used	242 g

Performance: See following log.

Performance:

		Amperes(a)			
Time	Volts	Reading	Actual	KW	Remarks
12:30	45	200	300	13.50	Start preheat on coke bed.
12:35	51	180	270	13.78	
12:40	42	170	255	13.26	
12:45	48	180	270	12.46	
12:50	47	180	270	12.70	
12:55	45	190	285	12.83	
1:00	45	190	285	12.83	Start charging around sidewalls. Load steady. Preheat 30 min.
1:05	41	220	330	13.53	Load picked up slightly.
1:10	40	200	300	12.00	Charging as required. Raise electrode slightly because of load pick up.
1:15	45	180	270	12.15	Crucible forming nicely. Arc almost covered.
1:20	47	170	255	12.00	Crucible O.K. Stoked slightly and covered. Crucible formation 20 min.
1:25	43	190	285	12.26	Stoked in and covered.
1:30	42	200	300	12.60	Stoked in and covered.
1:35	41	200	300	12.30	Seems to have more flame that Heat 1.
1:40	45	180	270	12.15	Stoked in and covered.
1:45	39	210	315	12.30	
1:55	40	200	300	12.00	Stoked in and covered.
2:05	40	200	300	12.00	Stoked in and covered.
2:15	40	200	300	12.00	Stoked in and covered.
2:20	40	200	300	12.00	
2:25	40	200	300	12.00	Stoked in and covered.
2:30	42	190	285	11.97	Stoked in and covered.
2:40	40	200	300	12.00	
2:45	40	200	300	12.00	All mixture in furnace.
3:00	45	180	270	12.15	Stoked in and covered.
3:05	45	180	270	12.15	
3:15	45	180	270	12.15	
3:17	45	180	270	12.15	Electrode freed. Power off. Metallic specks on electrode tip. Smelting time 117 min.

(a) Ampere factor X1.5 because of shunt.

Result: Crucible smaller than in Heat 1 but slightly thicker. Metal well collected at tip of electrode. Some metallic specks on wall of crucible.

Unreacted mixture	4100 g
Partially reacted and fused	2050 g
Metal - SiC - C 60 - 30 - 10	480 g
Metal	288 g

Comments: Figures for power consumption and electrode consumption not determined.

RECORD OF HEAT NO. 2

Date: 4/26/64

Materials: Coke 8 x 10 mesh (98% F.C.)

Gravel 8 x 10 mesh (99.5% SiO_2)

Mixture Order: Coke - 3264 g

Gravel - 8048 g

100% carbon theory

Preparation: Rolled in drum. Dumped on Floor and mixed just prior to charging.

Charging: By hand as required. Stoking as required.

Weights: Coke bed 300 g (4 x 6 mesh)

Electrode	-	Start	1800 g
		End	1583 g
		Used	217 g

Performance: See following log.

Performance:

Time	Volts	Amperes(a)		KW	Remarks
		Reading	Actual		
8:45	46	190	285	13.10	Start preheat on coke bed.
8:50	50	175	262	13.10	
8:55	51	170	255	13.00	
9:00	50	170	255	12.75	
9:05	47	190	285	13.40	
9:10	46	190	285	13.10	
9:15	45	200	300	13.50	Start charging around sidewalls slowly. Preheat 30 min.
9:20	42	200	300	12.60	Crucible forming.
9:25	43	190	285	12.25	
9:30	44	185	278	12.22	Crucible good size.
9:35	48	180	270	12.96	Arc covered. Crucible formation 20 min.
9:40	49	170	255	12.50	Nice gas pattern.
9:45	50	160	240	12.00	
9:50	50	170	255	12.75	Good gas pattern.
9:57					Lost load. Stoked in and picked up.
10:00	40	200	300	12.00	
10:10	45	190	285	12.80	Load fluctuating slightly.
10:20	43	170	255	10.97	
10:30	48	170	255	12.22	
10:40	45	190	285	12.81	
10:50	46	180	270	12.41	Worked as required.
11:00	47	170	255	12.00	
11:10	45	200	300	13.50	
11:20	48	170	255	12.25	Stoked in and covered.
11:30	50	170	255	12.75	All mixture not charged.
11:40	45	200	300	13.50	Electrode stuck. Power off. Smelting time 125 min.

(a) Ampere factor x 1.5 because of shunt.

Result: Crucible good size. Metal well collected at electrode tip. More metal visible on walls of crucible. Some whiskers at site of carbon particles.

Unused mixture	2500 g
Unreacted mixture	3768 g
Partially reacted and fused	2040 g
Metal - SiC - C 70 - 20 - 10	745 g
Metal	512 g

Comments: Figures for power consumption and electrode consumption not determined.

RECORD OF HEAT NO. 2a

Date: 4/30/64

Materials: Coke 8 x 10 mesh (98% F.C.)

Gravel 8 x 10 mesh (99.5% SiO_2)

Mixture Order: Coke - 2856 g

Gravel - 7042 g

100% carbon theory

Preparation: Rolled in drum. Dumped on floor and mixed just prior to charging.

Charging: By hand as required. Stoking as required.

Weights: Coke bed - 300 g (4 x 6 mesh)

Electrode	-	Start	1529 g
		End	1290 g
		Used	239 g

Performance: See following log.

Performance:

		Amperes(a)			
Time	Volts	Reading	Actual	KW	Remarks
7:10	45	200	300	13.50	Start preheat on coke bed.
7:15	47	190	285	13.40	
7:20	50	180	270	13.50	
7:25	49	180	270	13.22	
7:30	45	200	300	13.50	
7:35	48	180	270	12.96	
7:40	50	180	270	13.50	Start charging slowly around sidewalls. Preheat 30 min.
7:45	43	210	315	13.55	Crucible forming.
7:50	45	190	285	12.81	
7:55	44	200	300	13.20	Arc almost covered.
8:00	44	200	300	13.20	Crucible formation 20 min.
8:05	44	190	285	12.53	Nice gas pattern.
8:10	45	190	285	12.81	
8:15	44	190	285	12.53	Stoked in and covered.
8:20	45	200	300	13.50	
8:30	45	200	300	13.50	Stoked in and covered.
8:40	44	190	285	12.53	
8:50	43	200	300	12.90	Nice gas pattern.
9:00	44	190	285	12.53	Stoked in and covered.
9:10	44	190	285	12.53	
9:20	46	180	270	12.41	Stoked in and covered.
9:30	42	210	315	13.23	
9:40	45	190	285	12.81	
9:50	41	210	315	12.91	Stoked in and covered.
10:00	45	190	285	12.82	Large crucible. Furnace left to run to free electrode.
10:15	42	190	285	11.96	Electrode freed. Power off. Smelting time 135 min.

(a) Ampere factor x 1.5 because of shunt.

Result: Crucible good size. Metal well collected at electrode tip. Several metal whiskers on walls of crucible attached to carbon.

Unused mixture	1201 g
Unreacted mixture	3740 g
Partially reacted and fused	2160 g
Metal - SiC - C	800 g
70 - 20 - 10	560 g

Comments: Figures for power consumption and electrode consumption not determined.

RECORD OF HEAT NO. 3

Date: 3/13/64

Materials: Coke 100 mesh x down (97.5% F.C.)
Gravel 100 mesh x down (99.0% SiO_2)
Sugar binder (42.0% F.C.)
100% carbon theory

Mixture Order: Pellets 7455 g

Preparation: Mixtures of materials containing 2020 g gravel, 796 g coke, and 56 g sugar was blended in a muller for 10 minutes. 10% water was added and the mixture blended for another 10 minutes. Material was pelletized in a rotating ceramic ball mill with water added as it was required. Pellets were dried for 18 hours under heat lamps. Moisture content after drying was 0.1% H_2O.

Charging: By hand as required. Stoking as required.

Weights: Coke bed 300 g (4 x 6 mesh)

Electrode	-	Start	712 g
		End	572 g
		Used	140 g

Performance: See following log.

Performance:

		Amperes(a)			
Time	Volts	Reading	Actual	KW	Remarks
1:05	47	190	285	13.40	Start preheat on coke bed.
1:10	45	200	200	13.50	
1:15	45	200	300	13.50	
1:20	50	170	255	12.75	
1:25	47	180	270	12.69	
1:30	50	170	255	12.75	
1:35	51	160	240	12.25	Start charging around sidewalls. Preheat time 30 min.
1:40	35	220	330	11.56	Load picks up.
1:45	36	220	330	11.88	Arc almost covered.
1:50	44	190	285	12.53	Crucible open.
1:55	45	190	285	12.81	Cover arc. Crucible formation 20 min.
2:00	45	180	270	12.15	Stoked in and covered.
2:10	54	140	210	11.34	Lower electrode to pick up load.
2:20	46	170	255	11.72	Stoking seems to be much easier. No sticking around electrode.
2:30	44	170	255	11.22	Stoked in and covered.
2:40	45	170	255	11.48	Stoked in and covered.
2:50	45	170	255	11.48	Stoked in and covered. Seems to have more gas volume and fume.
3:00	46	170	255	11.72	Lost load and restored.
3:10	45	170	255	11.48	
3:20	45	170	255	11.48	
3:22	Power off. 87 minutes.				Lost load could not pick up.

(a) Ampere factor x1.5 because of shunt.

Result: Although run is short crucible was in good condition and metal was well collected. Since it is assumed that reduction rate is linear for all of smelting period this heat is useful.

Unreacted pellets	3808 g
Partially reacted and fused	1620 g
Metal - SiC - C 50 - 40 - 10	716 g
Metal	358 g

Comments: Figures for power consumption and electrode consumption not determined.

RECORD OF HEAT NO. 3a

Date: 3/14/64

Materials: Coke 100 mesh x down (97.5% F.C.)

Gravel 100 mesh x down (99.0% SiO_2)

Sugar binder (42.0% F.C.)

100% carbon theory

Mixture Order: Pellets 8815 g

Preparation: Same as for Heat No. 3.

Charging: By hand as required. Stoking as required.

Weights: Coke bed 300 g (4 x 6 mesh)

Electrode	-	Start	1255 g
		End	1108 g
		Used	169 g

Performance: See following log.

Performance:

		Amperes(a)			
Time	Volts	Reading	Actual	KW	Remarks
10:50	45	200	300	13.50	Start preheat on coke bed.
10:55	46	190	285	13.12	
11:00	54	160	240	12.97	
11:05	52	170	255	13.27	
11:10	48	180	270	12.96	
11:15	52	160	240	12.49	
11:20	44	170	255	11.21	Start charging around side-walls. Preheat time 30 min.
11:25	40	200	300	12.00	
11:30	41	220	330	13.52	Arc almost covered.
11:35	43	190	285	12.25	
11:40	44	190	285	12.53	Crucible forming nicely. Cover arc. Crucible formation 20 min.
11:50	44	190	285	12.53	Stoke and feed as required.
12:00	41	200	300	12.30	
12:10	40	200	300	12.00	Electrode free most of time.
12:20	38	210	315	12.96	Very easy to stoke and cover.
12:30	40	200	300	12.00	
12:40	40	200	300	12.00	
12:50	40	210	315	12.60	Very easy to maintain mixture level.
1:00	40	200	300	12.00	Nice gas pattern.
1:10	40	190	285	11.40	Not so much fume this heat.
1:20	45	180	270	12.15	Stokes very easily.
1:30	39	210	315	12.29	
1:40	40	190	285	11.40	
1:50	42	190	285	11.96	Mixture level easily maintained.
2:00	42	200	300	12.60	Electrode free. Power off. Smelting time 140 min.

(a) Ampere factor x 1.5 because of shunt.

Results: Very good heat. Pellets do not stick around electrode and mix level easily maintained. Metal well collected.

Unreacted pellets	4107 g
Partially reacted and fused	1642 g
Metal - SiC - C 70 - 20 - 10	956 g
Metal	669 g

Comments: Figures for power consumption and electrode consumption not determined.