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SOME RELATIONSHIPS IN THE SYSTEM  
ZIRCONIA-FERROUS OXIDE-SILICA

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## SOME RELATIONSHIPS IN THE SYSTEM $ZrO_2$ -FeO- $SiO_2$

### INTRODUCTION

Although there is little, if any, geological interest in the system zirconia-ferrous oxide-silica, this system is becoming of increasing importance in metallurgical and ceramic fields. With the increasing use of zircon and zirconia refractories at high temperatures, under conditions in which contact with slags rich in ferrous oxide might be expected, it is important to learn more about this system. One application in which the above conditions are met is in the foundry. In certain types of castings in which surface condition and dimensional tolerance are very important, shell molds made of zircon sand are used. Although in general little slag as such is encountered in this operation, ferrous oxide may be formed at the interface between the molten metal and the mold. This ferrous oxide may be in contact with the refractory for periods of time up to several minutes or more at temperatures in excess of 1200°C. Another application in which zircon refractories have been used is in the front and back walls of open hearth furnaces. Here the refractory may be in contact with slags of varying ferrous iron content for long periods of time also at temperatures above 1200°C. Zirconia refractories, as well as zircon refractories, are used in induction furnace linings, laboratory furnace muffles, crucibles, and other kiln furniture, all at times may be under conditions in which ferrous oxide is encountered at high temperatures.

In general, three types of information about the  $ZrO_2$ -FeO-SiO<sub>2</sub> system will be useful for the judicious use of zircon and zirconia refractories: (1) phase equilibrium relationships in the binary and ternary systems; (2) data on the kinetics of reaction and phase changes in the system; (3) thermodynamic information such as activity coefficients, heats of formation, free energy relationships. The present work is concerned with the first of these three general areas.

A survey of the literature has shown that the three component oxides and the two normally stable binary compounds have been well investigated. There are still a few regions in which agreement is not complete, but except for these few the agreement is good. The three limiting binary systems have been investigated, but some questions still remain.

The silica phases in the one component system SiO<sub>2</sub> have been under investigation for many years by many investigators and there are still a number of unresolved questions about this intriguing oxide. However, except to note that even in this well investigated one component system work remains to be done in order that a complete understanding may be gained, further discussion will not be made.

Wustite (FeO) has also been studied by many investigators from many viewpoints (1-5)\*. It was early discovered that the stoichiometric compound FeO does not exist<sup>(1)</sup>. There is always a deficiency of iron positions in the lattice with electrical neutrality being maintained by

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\* References at end of paper.



the presence of ferric as well as ferrous ions. This, of course, complicates any system in which wustite is a component, for it means that ferric iron as well as ferrous iron can exist in equilibrium with metallic iron. It also means that wustite can be considered a single component only if the ferric iron is ignored. The iron-oxygen system as reported by Darken and Gurry<sup>(3,4)</sup> is that which is most universally accepted. They show that the composition of wustite can vary from 23.2 percent oxygen to 25.5 percent oxygen at 1375°C. The composition at 560°C is 23.3 percent oxygen, below which wustite can exist only in a metastable condition. Consequently, the composition of wustite in any particular specimen will depend upon a number of factors such as the temperature from which it was quenched and the atmosphere in which it was heated and quenched.

Zirconia ( $ZrO_2$ ), which occurs in nature as the monoclinic mineral baddeleyite, has also been investigated by a number of workers, some of which are listed in the bibliography<sup>(6-21)</sup>. Some questions still remain in certain aspects of the monoclinic-tetragonal transformation, and on the existence of a cubic phase above 1900°C. Blumenthal<sup>(21)</sup> gives the names "ruffite" to the tetragonal phase, and "arkelite" to the cubic phase. However, since these phases have not been found in nature, their use as mineral names should be discouraged. From the work of Curtis, Donney, and Johnson<sup>(22)</sup>, it appears that the high temperature cubic phase can be present only if there is some impurity present which can cause this phase to prevail. In the high purity zirconia they found the

tetragonal phase to be stable from just above 1000°C all the way to the melting point at 2700°C.

The three limiting binary systems FeO-SiO<sub>2</sub>, ZrO<sub>2</sub>-SiO<sub>2</sub>, and FeO-ZrO<sub>2</sub> have all been investigated to some extent. The work of Bowen and Schairer<sup>(1)</sup> in the system FeO-SiO<sub>2</sub> has remained essentially unchallenged since it was published in 1932. Part or all of it has been rechecked by a number of workers, most recently by Schuhmann and Ensio<sup>(23)</sup> and by Allen and Snow<sup>(24)</sup>, who showed a flexure in the wustite liquidus but made no other changes. The system contains one stable binary phase fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) and a region of liquid immiscibility on the silica-rich end. Another binary phase "ferrosilite" (FeSiO<sub>3</sub>) is reported in this system by Bowen<sup>(25)</sup> but no region of stability has been positively shown for this phase. Bowen was not able to cause this phase to precipitate out of a glass of the stoichiometric composition. Schairer and Yagi<sup>(26)</sup> also Roedder<sup>(27)</sup> had results similar to Bowen's. Rigby<sup>(28)</sup>, however, reported ferrosilite may be encountered when a 1:2 ferrous oxide-silica mixture is heated to 1350°C. Ferrosilite was not encountered under the conditions of the present investigation.

In the ZrO<sub>2</sub>-SiO<sub>2</sub> system there is somewhat less agreement among the various investigators. However, since this will be discussed further in a later section, an attempt will not be made to pursue it in detail at this point. In this system there is one binary oxide compound zircon (ZrSiO<sub>4</sub>). The effects of ferrous oxide, either as such, or, combined with silica

upon this compound forms one of the major parts of this investigation.

The system  $\text{FeO-ZrO}_2$  has been studied to a lesser extent than any of the other limiting systems. Recently, Fischer and Hoffmann<sup>(20)</sup>, in Germany, have presented a diagram of the system in the temperature range of from  $1300^\circ\text{C}$  to  $1800^\circ\text{C}$  which includes the eutectic region. Since the present results did not exactly match their results, further discussion will be postponed until a later section. No compounds have been found in this system.

Therefore, in the three limiting systems, only two binary compounds, fayalite and zircon, are found which have proven regions of stability.

This investigation is chiefly concerned with relationships in the ternary system  $\text{FeO-ZrO}_2\text{-SiO}_2$ . The following general areas have been considered: (1) compatibility relationships in the ternary system, (2) binary joins, (3) ternary compounds, (4) ternary invariant points, (5) fields of primary crystallization, (6) effect of  $\text{HfO}_2$  and other impurities on the monoclinic-tetragonal transformation of  $\text{ZrO}_2$ , (7) dissociation of zircon and (8) region of liquid immiscibility.

## MATERIALS AND EXPERIMENTAL WORK

The sources and compositions of the materials used in this investigation are summarized in Table I. Figure 1 shows the mix compositions investigated.

Most of the experimental work was done in one of two furnaces. Both are horizontal tube furnaces heated with silicon carbide elements. One furnace was controlled by a total off-on type controller, and the other furnace was controlled by a saturable reactor unit. The compatibility studies and the preliminary field boundaries were done in the former furnace. The work demanding more precise temperature control was done in the furnace controlled by the saturable reactor.

Because wustite is not stable in an air atmosphere, and becomes oxidized to magnetite in air at elevated temperature, it was necessary to fire the samples in an environment in which wustite is stable. This was accomplished in one of two ways.

(1) In the compatibility studies, discs one centimeter in diameter by about 5 millimeters thick were fired in an atmosphere of 50 percent carbon monoxide and 50 percent carbon dioxide. It has been established that wustite is stable in this atmosphere in the temperature ranges which were used. (2)

(2) Wustite is compatible with iron, therefore iron crucibles could be used for temperatures up to 1500°C. Since all of the invariant

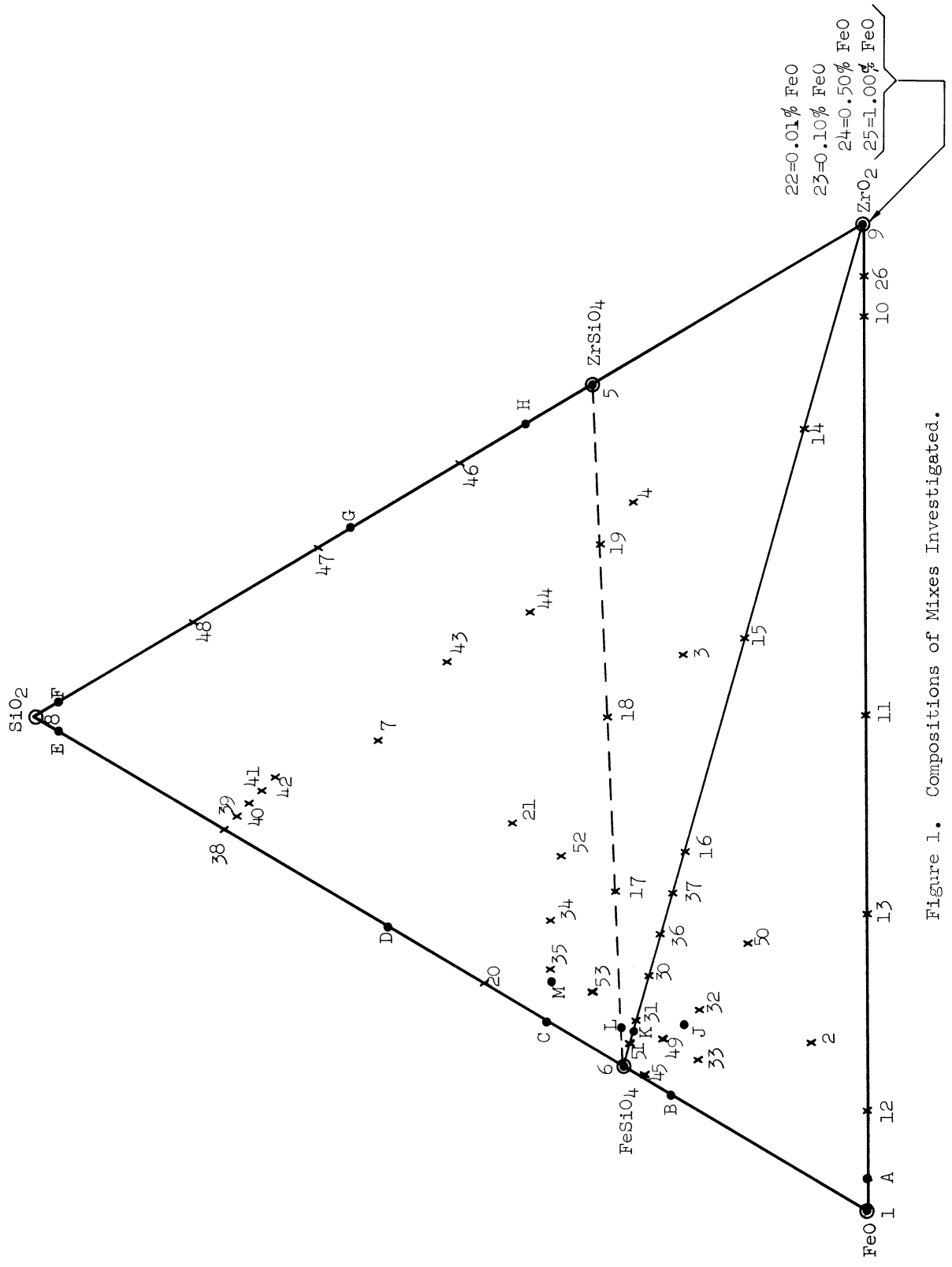


Figure 1. Compositions of Mixes Investigated.

points investigated in this ternary system are well below 1500°C, iron crucibles with tightly fitting plugs were used for determining these points and for locating phase field boundaries (Figures 2 through 6). Figure 6 shows the furnace set-up used in the quenching experiments and for the differential thermal analysis work. Table II gives the chemical analysis of the Ferrovac "E" rod used for the crucibles and plugs. In the runs where the charge became mostly molten, it was found to be necessary to weld around the top of the crucible and plug to keep the liquid in the crucible. It was also found necessary to press the plugs into the crucible in an inert atmosphere to preclude the possibility of increasing the FeO content of the charge because of reaction of entrapped oxygen with the iron crucible. This was accomplished by enclosing the loaded crucible, with the plug to one side, in a pliable polyethylene bag. A piece of vacuum tubing and a short length of steel rod were inserted into the opening of the bag and the opening sealed shut around them. The bag was evacuated and flushed repeatedly (at least five times) with purified argon, or helium. The gas was purified by passing it over calcium chips at 1000°C and copper gauze at 600°C. The plug was placed on the crucible and pressed into place with the steel rod in a Carver press. The crucible was then removed from the bag.

In order to determine the most effective quenching medium, a

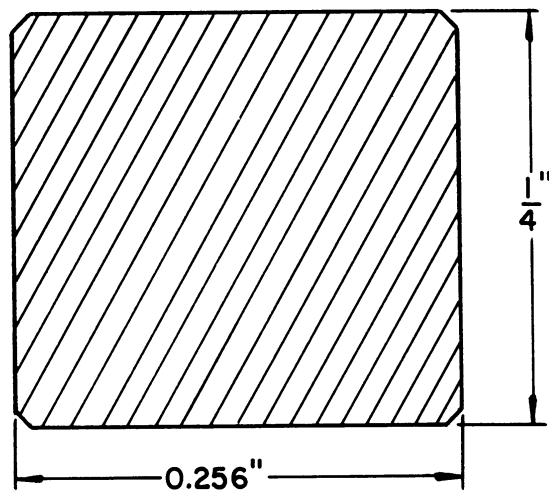
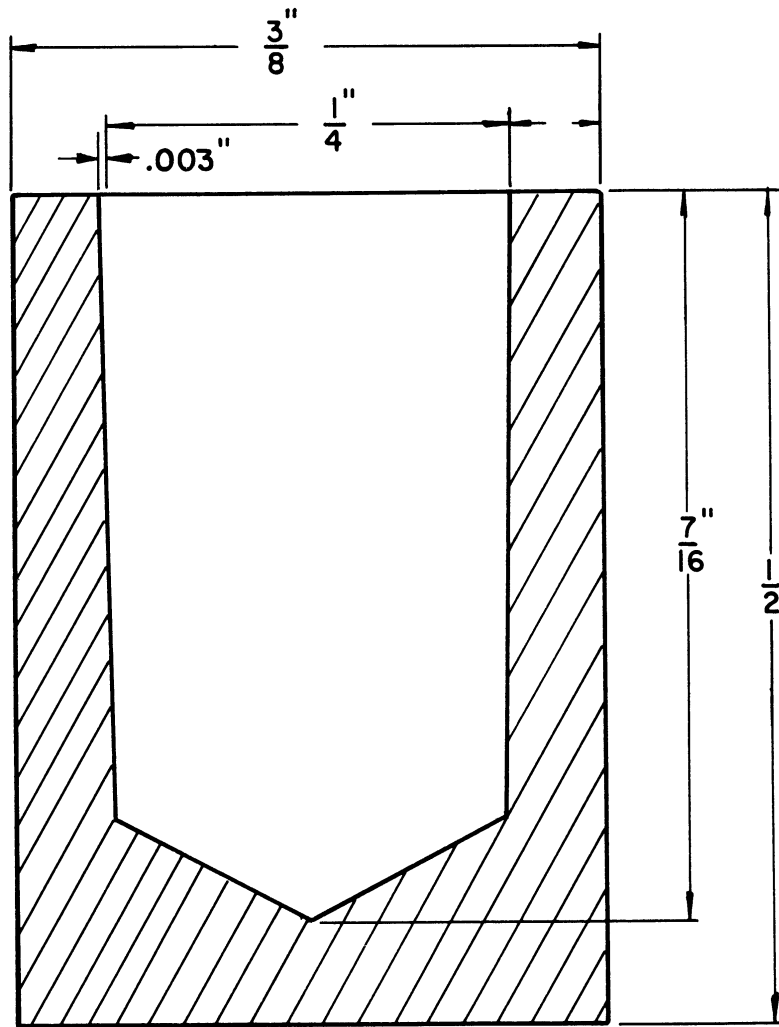


Figure 2. Iron Crucible and Plug from  $\frac{3}{8}$ " Ferrovac "E" Rod.

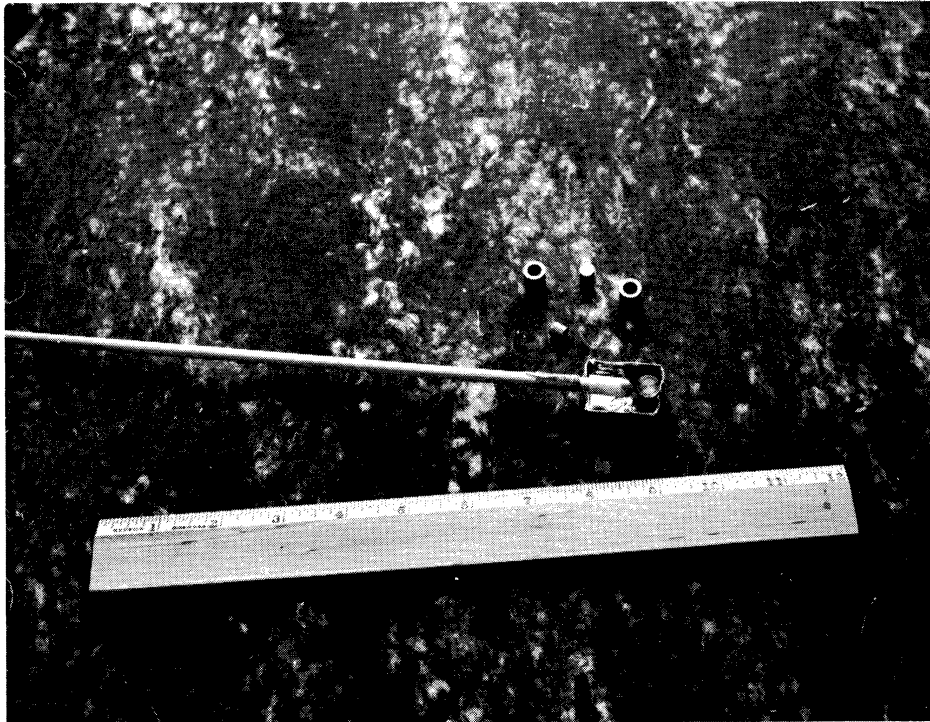


Figure 3. Crucibles and Apparatus for Quenching Experiments.

Empty crucibles and plugs above. Platinum vessel, thermocouple, and loaded crucible ready to be placed in the furnace, below.



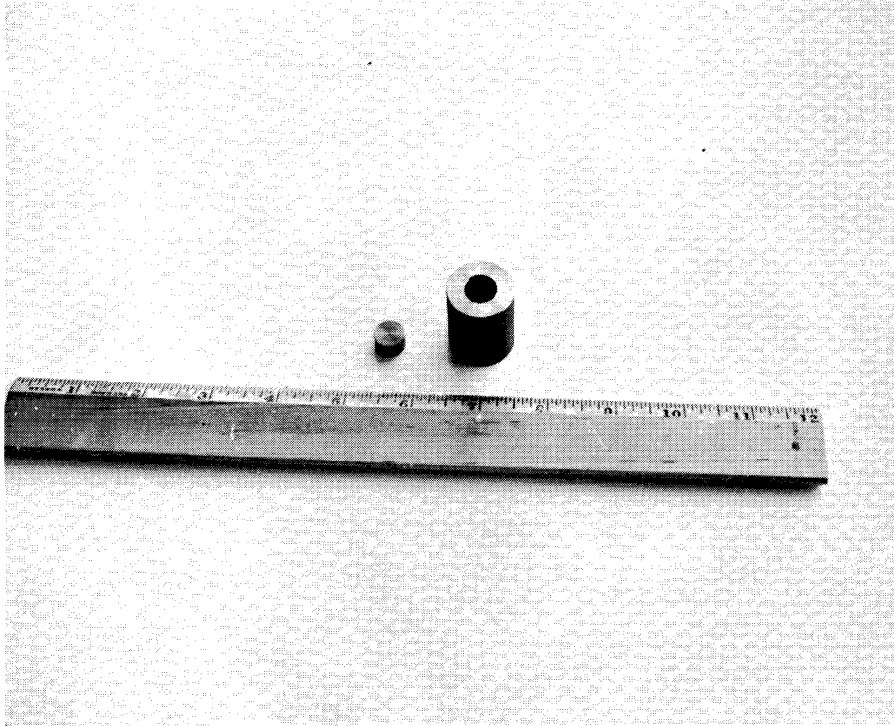


Figure 4. Large Iron Crucible and Plug.

Crucibles of this type were used to make samples for chemical, X-ray, and microscopic analysis.

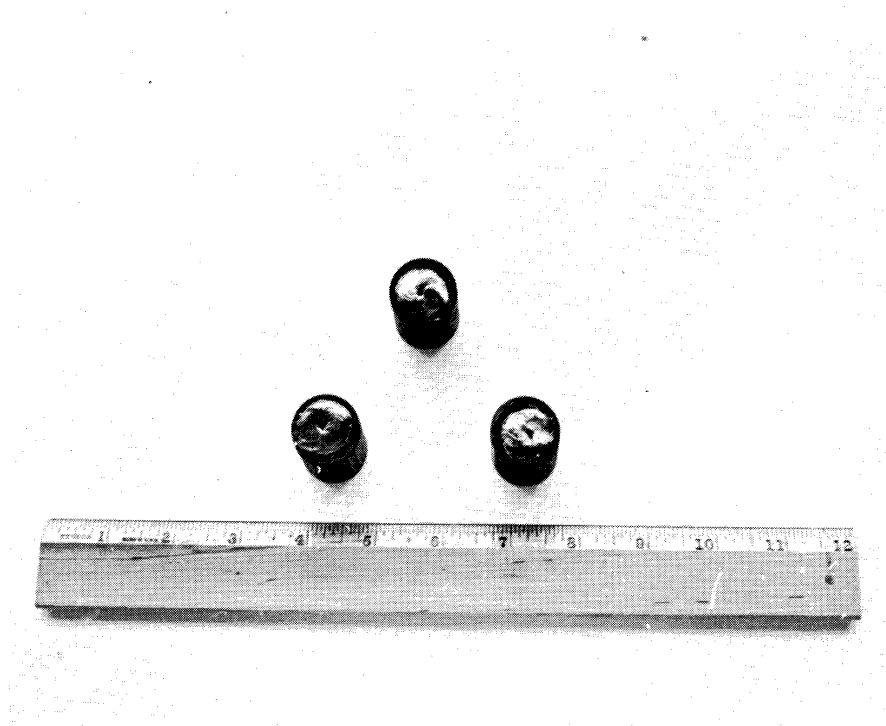


Figure 5. Large Iron Crucibles Loaded, Plugged, and the Tops Welded Ready to be Fired.

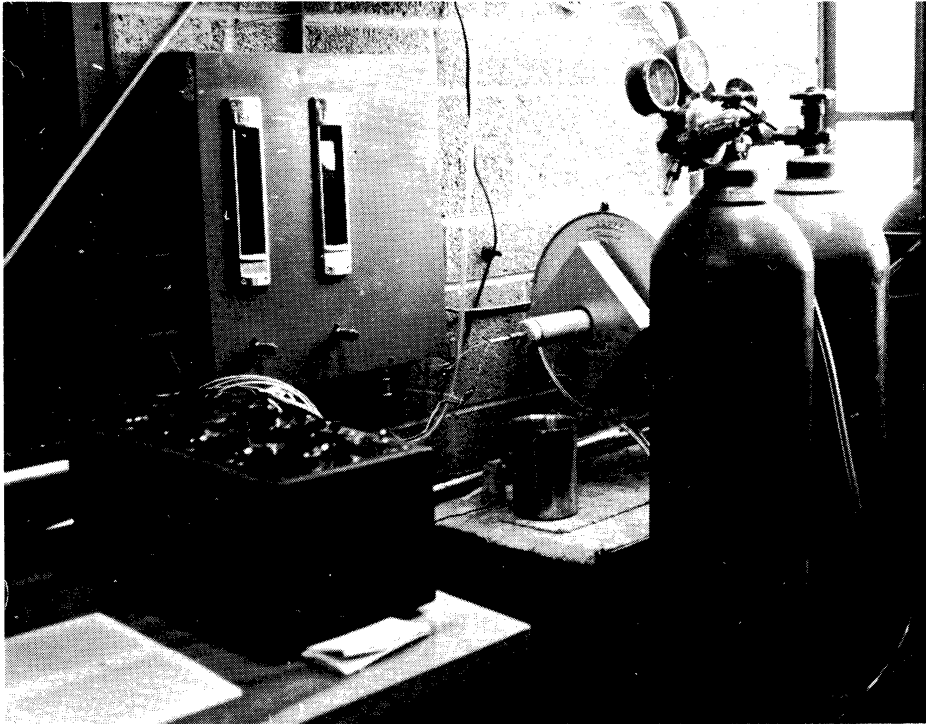


Figure 6. Furnace, Temperature Measuring, Quenching, and Atmosphere Apparatus for the Quenching Experiments.

series of tests was performed by embedding a thermocouple in the center of a piece of iron of about the same mass as the crucible. This piece of iron was heated to 1200°C then quenched in the medium. Various media were checked including water, mercury(specimen submerged), and mercury (specimen floating), various oils and gases. It was found that the most severe quenching was obtained with water. The tests were repeated by embedding the thermocouple in a piece of silica brick. Again it was found that water gave the most severe quench. This information is summarized in Table III.

The study of the immiscible liquid regions was accomplished by pressing small cylinders of the appropriate compositions (1/8 inch in diameter by approximately 1/8 inch high) in a steel die. The top surface of the cylinders was melted in a natural gas-oxygen flame and quenched with a stream of water.

Phase identification in this investigation was accomplished by means of transmitted and reflected light microscopy<sup>(5)</sup> and by X-ray diffraction.

## RESULTS AND DISCUSSION

### Compatibility Relationships

In the ternary system  $\text{FeO-ZrO}_2\text{-SiO}_2$ , if we assume first that there are no ternary compounds, there are at most three possible compatibility

regions. Because of the dissociation of zircon in the solid state, it seems likely that there will be only two regions at the liquidus surface. These two will then most probably be  $\text{FeO-Fe}_2\text{SiO}_4\text{-ZrO}_2$  and  $\text{ZrO}_2\text{-Fe}_2\text{SiO}_4\text{-SiO}_2$ . The present compatibility study has verified these expectations by showing that there are no ternary compounds in the system and that zirconia and fayalite are compatible forming a binary system. Below about  $1550^\circ\text{C}$  fayalite and zircon are also compatible and three compatibility regions are found. These three regions are  $\text{FeO-Fe}_2\text{SiO}_4\text{-ZrO}_2$ ,  $\text{Fe}_2\text{SiO}_4\text{-ZrSiO}_4\text{-ZrO}_2$ , and  $\text{Fe}_2\text{SiO}_4\text{-ZrSiO}_4\text{-SiO}_2$ . It may be noted that fayalite is at one apex of each compatibility triangle. The two compatibility systems are shown in Figure 7. The overall results are summarized in Figure 8.

The arrangement of the three compatibility triangles in the ternary system has a direct effect upon the behavior of zircon sand in the presence of ferrous oxide. It may be seen from Figure 8 that an addition of approximately 15 percent of wustite to zircon would cause a marked dissociation of the zircon at, for instance,  $1200^\circ\text{C}$  with the formation of fayalite. It may also be seen that if about 44 percent of wustite is added to zircon at  $1200^\circ\text{C}$  the zircon would be completely dissociated with about 62 percent fayalite and 38 percent of baddeleyite resulting on cooling. Figures 9-A, B, and C illustrate the phase compositions which are found at three points along the line between zircon and wustite. These represent two of the three compatibility triangles. The third is

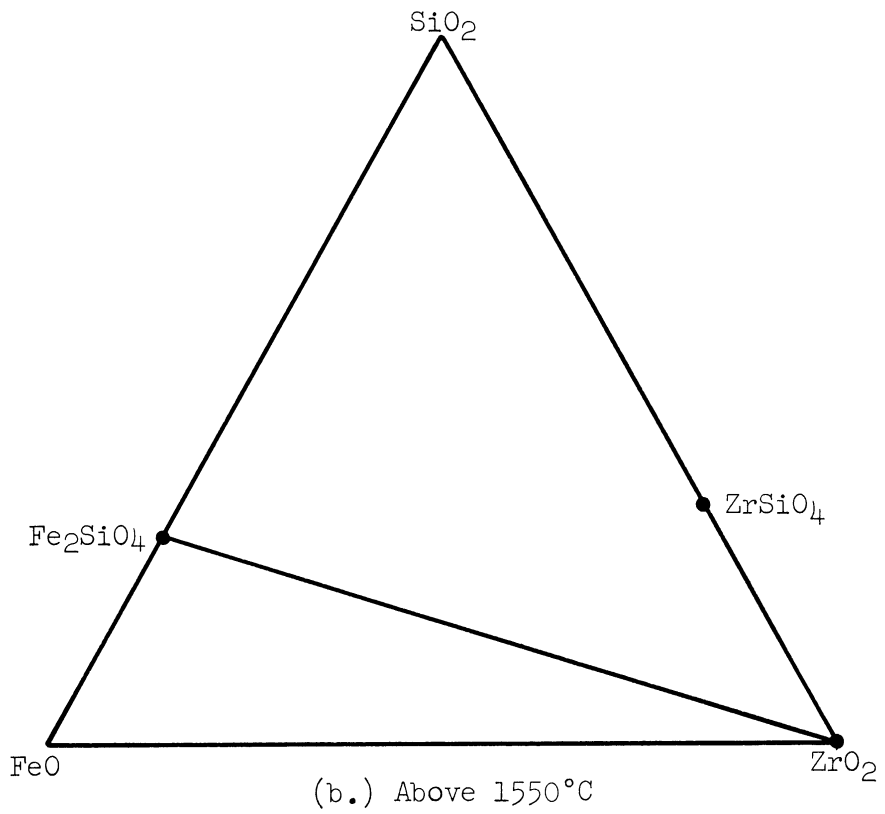
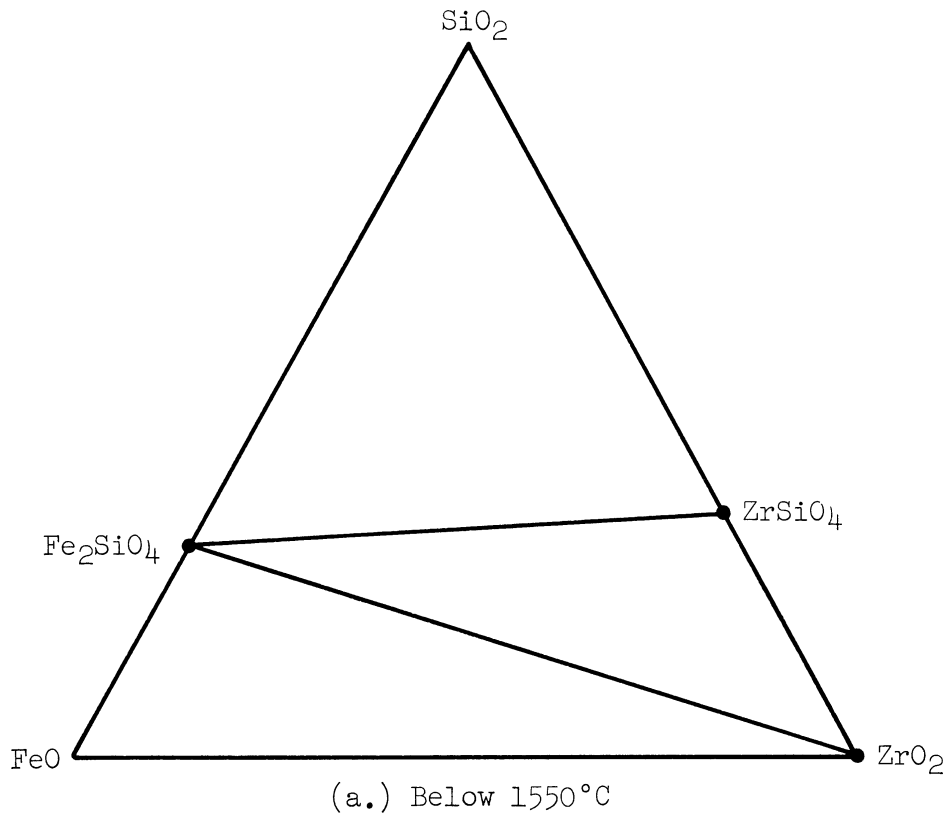


Figure 7. Compatibility in the System FeO-ZrO<sub>2</sub>-SiO<sub>2</sub>.

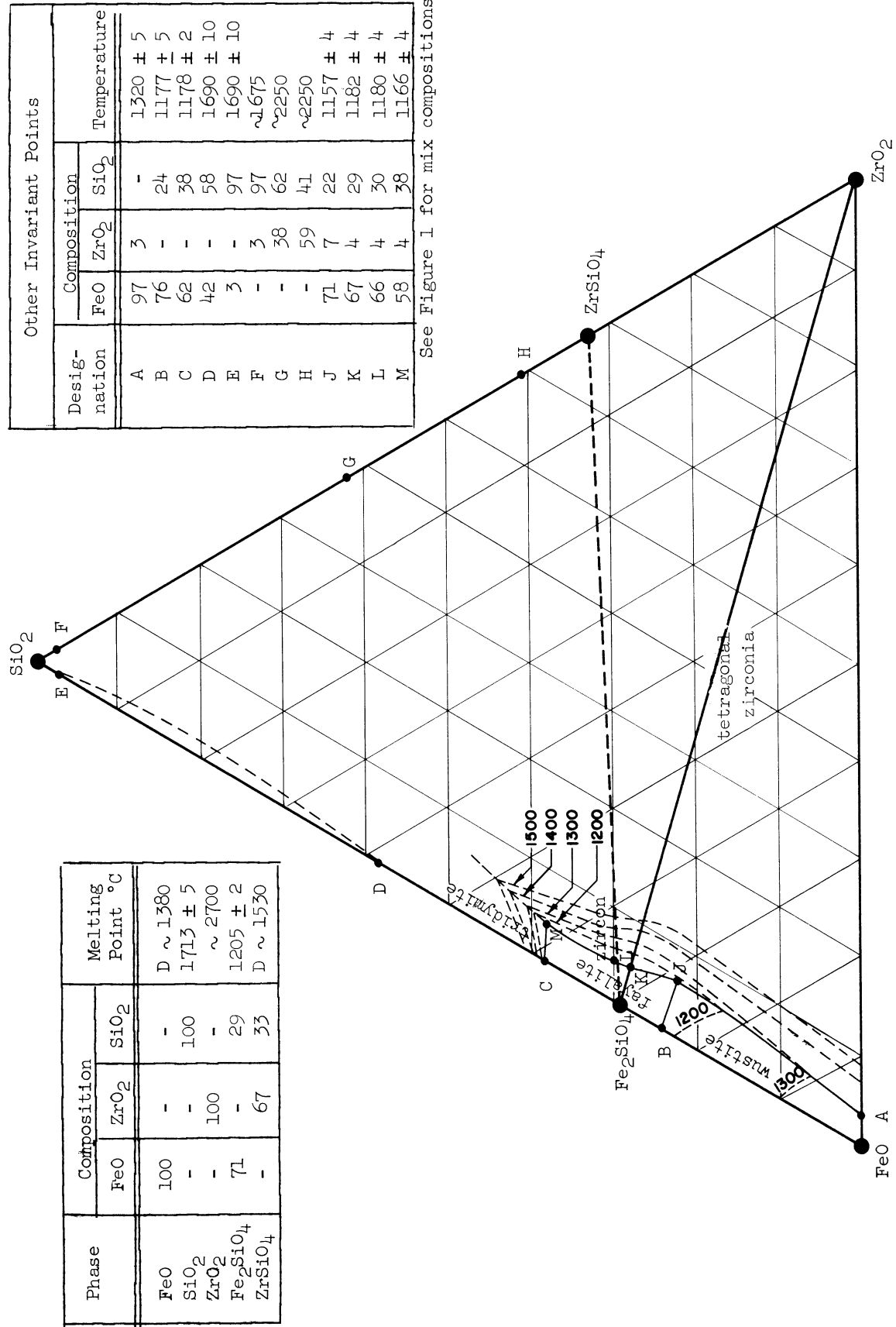


Figure 8. The System FeO-ZrO<sub>2</sub>-SiO<sub>2</sub>

represented by Figure 9-D. The compositions in Figure 9 have all been heated to 1200°C in an atmosphere of 50/50 CO/CO<sub>2</sub> and quenched in water. None was completely melted, although of course some contained more liquid at this temperature than others. For instance, the diagram for the system, Figure 8, shows that the composition of mix 2 (Figure 9-A) would be approximately 1/3 liquid at 1200°C while mix 4 would contain about half that amount of liquid at the same temperature. The photomicrographs show the phases present, but do not necessarily show the proper relative phase quantities for the mix composition as a whole.

#### Binary Systems and Joins

In the ternary system there are four binary systems, the three limiting binary systems, and the join ZrO<sub>2</sub>-Fe<sub>2</sub>SiO<sub>4</sub>. The join Fe<sub>2</sub>SiO<sub>4</sub>-ZrSiO<sub>4</sub> is not a binary system at all temperatures because of the dissociation of zircon in the solid state to ZrO<sub>2</sub> and SiO<sub>2</sub>. The limiting systems have all been studied previously although there is not universal agreement on all points. The FeO-SiO<sub>2</sub> system was worked out by Bowen and Schairer<sup>(1)</sup> (shown in Figure 10). The system FeO-ZrO<sub>2</sub> as reported recently by Fischer and Hoffman<sup>(29)</sup> is shown in Figure 11. These authors report a binary system with a single eutectic at about 3 percent of ZrO<sub>2</sub> and at 1330 ± 15°C. They also report a solubility of about 4 percent of FeO in the tetragonal form of ZrO<sub>2</sub> at 1450°C.





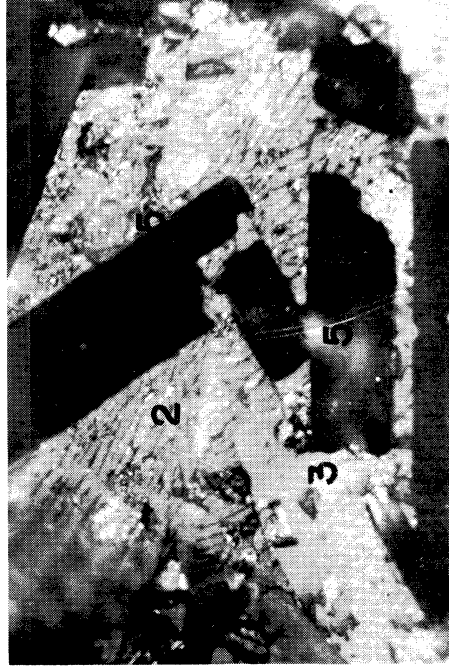
A. Mix 2



B. Mix 3



C. Mix 4



D. Mix 7

Figure 9. Photomicrographs Illustrating the Three Compatibility Regions Present at 1200°C.

(1) Wustite, (2) Fayalite, (3) Zircon, (4) Baddeleyite, (5) Tridymite, (6) Glass.

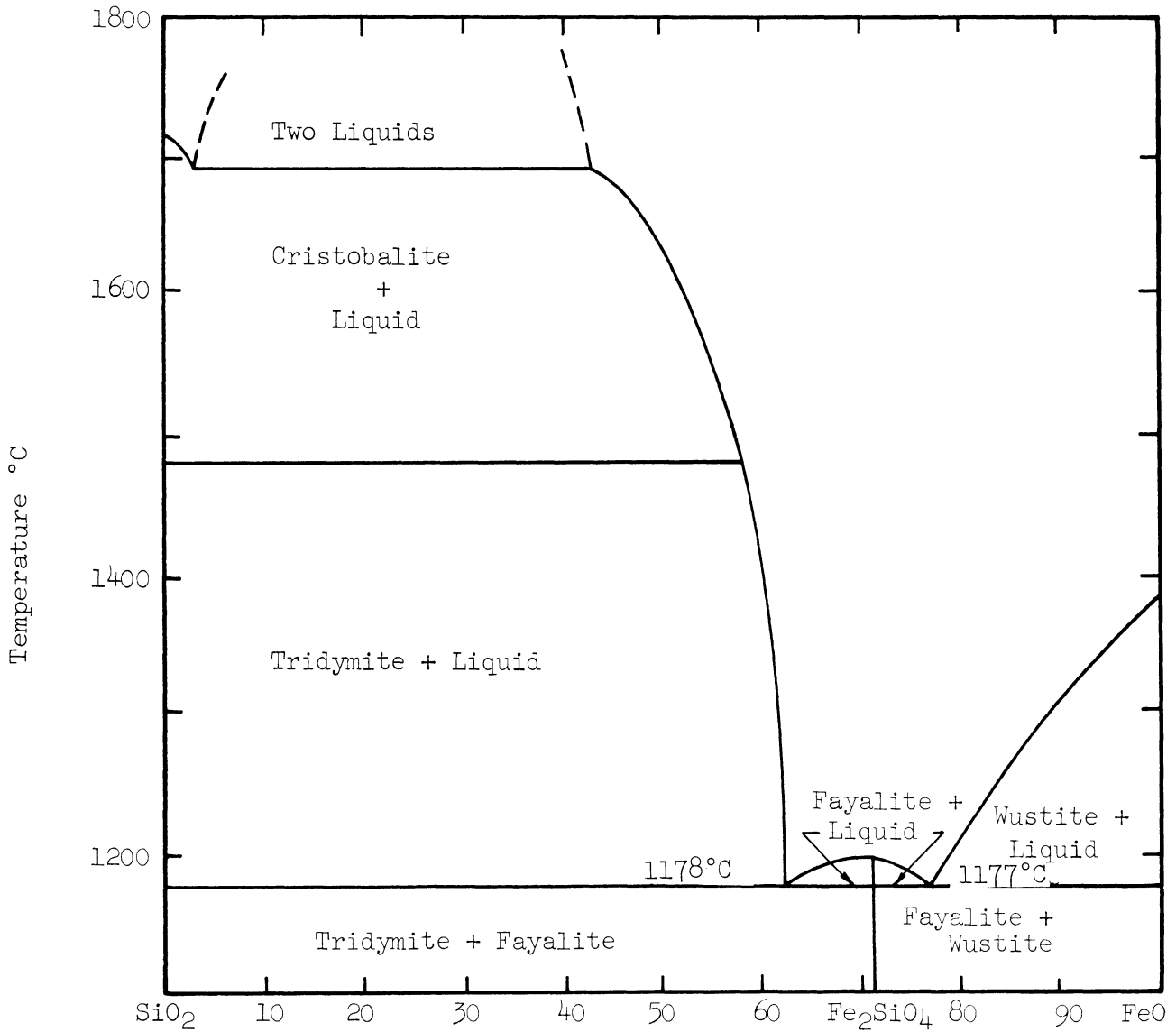


Figure 10. Equilibrium Diagram of the System FeO-SiO from N. L. Bowen, J. F. Schairer.

Am. Jour. Sci., 4, 177-213 (1932).

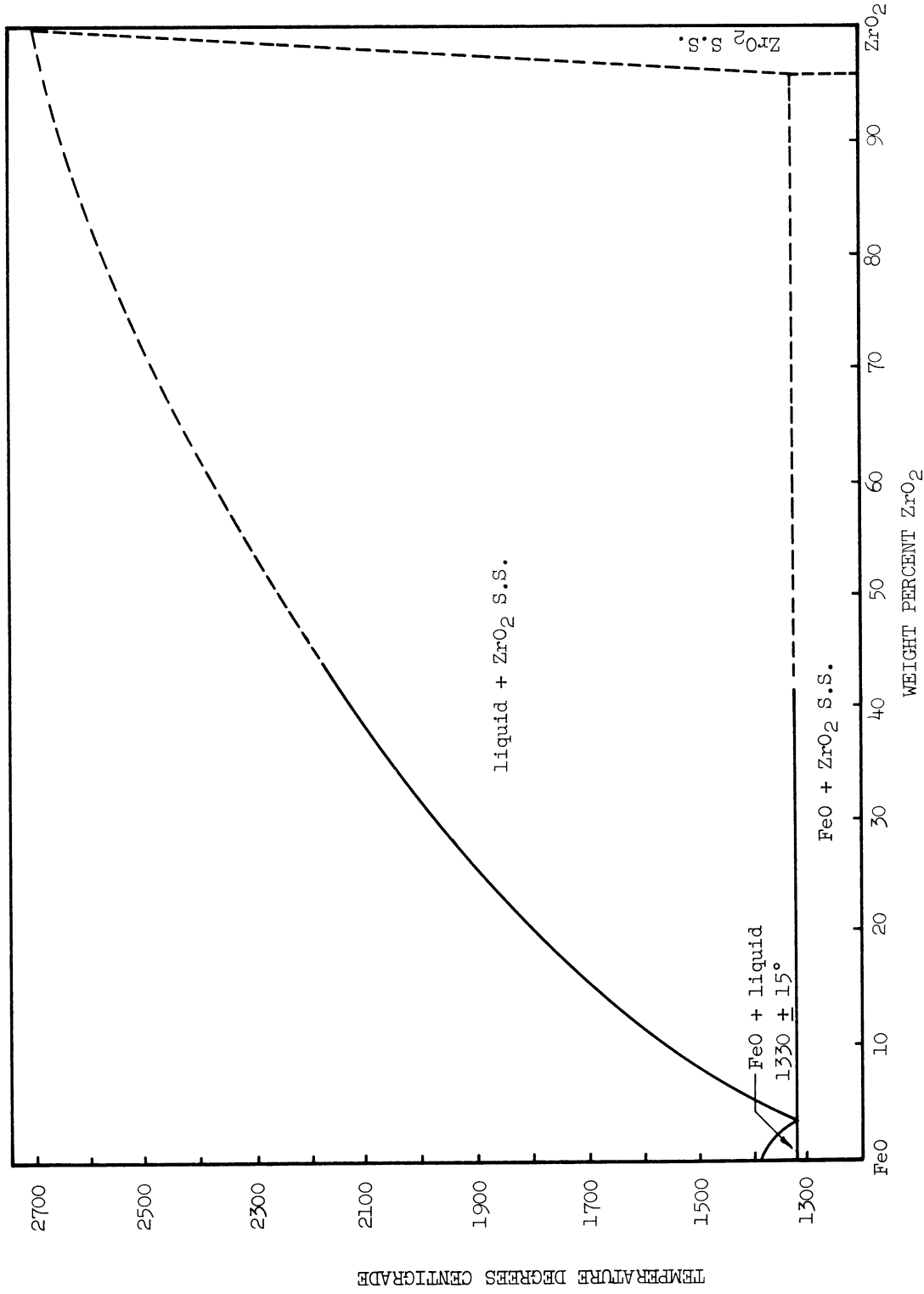


Figure 11. The System FeO-ZrO<sub>2</sub> according to W. A. Fischer and A. Hoffman.

Arch. Eisenhüttenw., 28, 739-743 (1957).

Quenching experiments to check this work have shown the eutectic to be less than 5 percent  $ZrO_2$  and probably about 3 percent as they reported. The eutectic temperature, however, was found to be  $1323 \pm 3^\circ C$ . Careful measurements in the back reflection region of mixes of  $ZrO_2$  with concentrations of 0.01, 0.10, 0.50, 1.00, and 5.00 percent of FeO, quenched from  $1500^\circ C$  after 1 hour showed only the monoclinic phase with no detectible shift in lattice lines. No evidence of exsolution was observed in the microsections examined by optical and electron microscopes.

Fischer and Hoffman based their conclusion of the solubility of FeO in  $ZrO_2$  at  $1800^\circ C$  upon the observation that after heating a sample of  $ZrO_2$  containing 3 percent of FeO at  $1800^\circ C$  in argon and quenching in water, no wustite was detectable microscopically or by means of X-ray diffraction. They state further that this "solid solution" does not decompose upon heating at  $1350^\circ C$  to  $1450^\circ C$  for several hours. Their observations do not necessarily mean that the FeO has gone into solid solution, however, for at temperatures of  $1800^\circ C$  in an atmosphere of argon it is entirely possible that the FeO could have been lost by vaporization, or by the draining away of liquid oxide. On the other hand, if the FeO had gone into solution in the tetragonal phase as they suggest, and there is very little or no solubility of FeO in the monoclinic phase, as they also suggest, then there should be evidence of an exsolution phase in the zirconia grains.

In order to check this possibility, a mixture of  $ZrO_2$  with 5 percent by weight of wustite was pressed into a cylinder  $1/8$  inch in diameter by  $1/4$  inch high at 5000 psi, placed in a stabilized zirconia crucible in a graphite susceptor and heated in a nitrogen atmosphere by induction to a little over  $1800^\circ C$  for 1 hour. The sample was allowed to cool in the furnace. Although the sample cooled to a black heat in a little less than 10 minutes, any exsolution phase formed would be large enough to be visible under the microscope. No evidence of exsolution was observed at a magnification of 1000. The sample, when it was removed from the crucible, was filled with cracks parallel to the long axis of the cylinder, but considerable sintering had taken place. Several pieces of the specimen were mounted in bakelite and polished for microscopic examination, and powder specimens were prepared for X-ray diffraction analysis. Microscopic examination of the polished specimen showed that complete recrystallization of the zirconia had occurred. In samples fired at temperatures up to  $1600^\circ C$  the zirconia grains appeared as rounded to irregular particles in a matrix which appeared smooth, or occasionally contained a eutectic structure. In the sample fired to  $1800^\circ C$ , the zirconia grains appear as small cigar shaped particles in a smooth matrix, the reflectivity of which appears to be nearer to that of zirconia than that of the samples heated at lower temperatures. (See Figure 12.) This can be explained either as an increase of reflectivity of the zirconia because of iron in

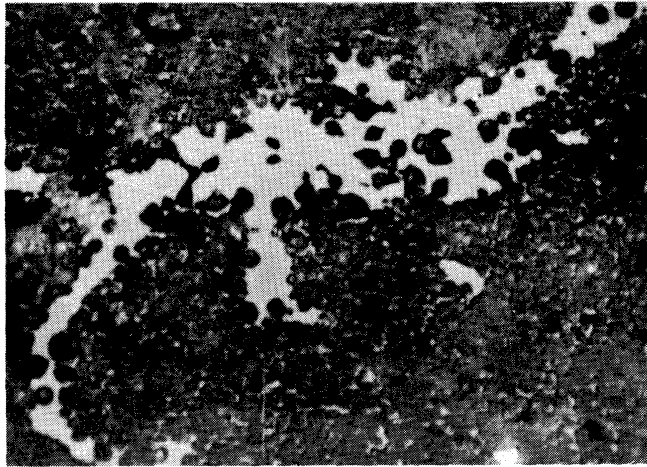


Figure 12. Mix 26 ( $ZrO_2 + 5\% FeO$ ).  
1500°C for 1 hour. 1000X Magnification

solution in the zirconia or as in increase of zirconia in solution in the matrix phase which would lower the reflectivity of the matrix making it nearer that of the zirconia. Electron microscope examination of polished surfaces of the material fired at 1800°C for 1 hour and furnace cooled revealed no evidence of a precipitate within the zirconia grains, confirming light-microscope examinations. X-ray diffraction patterns showed only the monoclinic zirconia lines with no detectable shift in lattice lines. Thus, it seems doubtful that any appreciable solubility of FeO in ZrO<sub>2</sub> exists up to 1800°C.

A number of studies have been made of the system ZrO<sub>2</sub>-SiO<sub>2</sub> of which three seem the most deserving of mention: Gellar and Lang<sup>(30)</sup>, Curtis and Sowman<sup>(31)</sup>, and Toropov and Galakov<sup>(32)</sup> (Figures 13, 14 and 15). Gellar and Lang reported a eutectic at about 3 percent ZrO<sub>2</sub> and at 1675°C. They show zircon to dissociate to ZrO<sub>2</sub> plus a liquid at about 1775°C and a solubility of SiO<sub>2</sub> in ZrO<sub>2</sub> of approximately 10 percent by weight. Earlier work by Washburn and Libman<sup>(33)</sup> and by Zirnova<sup>(34)</sup> had reported a true melting temperature for zircon at 2550°C and 2430°C respectively. Curtis and Sowman show the eutectic at 3 percent ZrO<sub>2</sub> and 1675°C and also the SiO<sub>2</sub> solubility in ZrO<sub>2</sub> at 10 percent, but they show zircon to dissociate to ZrO<sub>2</sub> and silica in the solid state at about 1530°C. Toropov and Galakov agree with Curtis and Sowman on all of these points, but they report a region of two immiscible liquids in the region of 62 percent to 41 percent of SiO<sub>2</sub> at 2250°C. Barlett<sup>(34)</sup> also

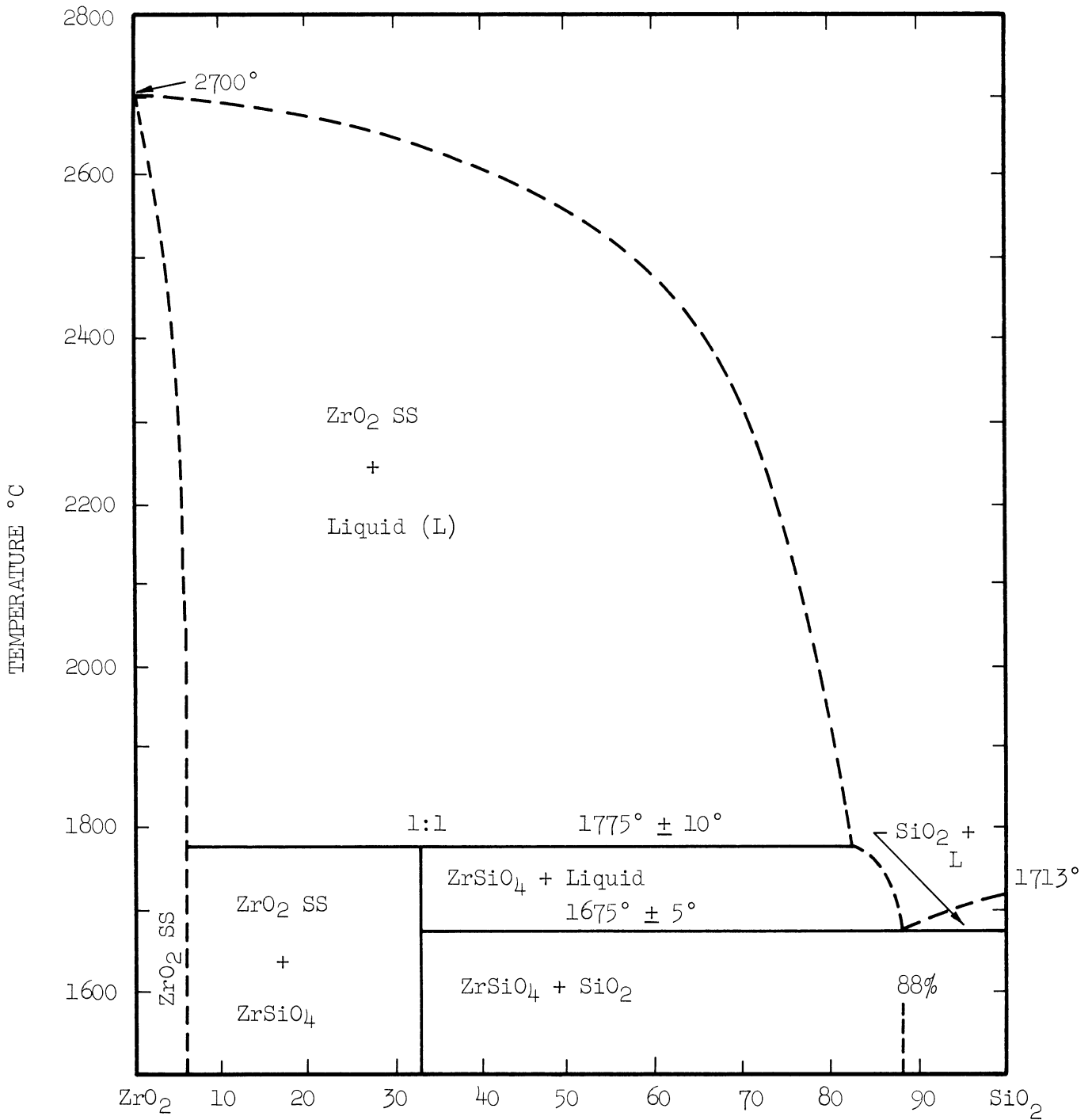


Figure 13. ZrO<sub>2</sub>-SiO<sub>2</sub> from R. F. Geller, S. M. Lang, Nat. Bur. of Standards.

Revised and corrected phase diagram, Phase Diagrams for Ceramists (1956), figure 132, p. 67.



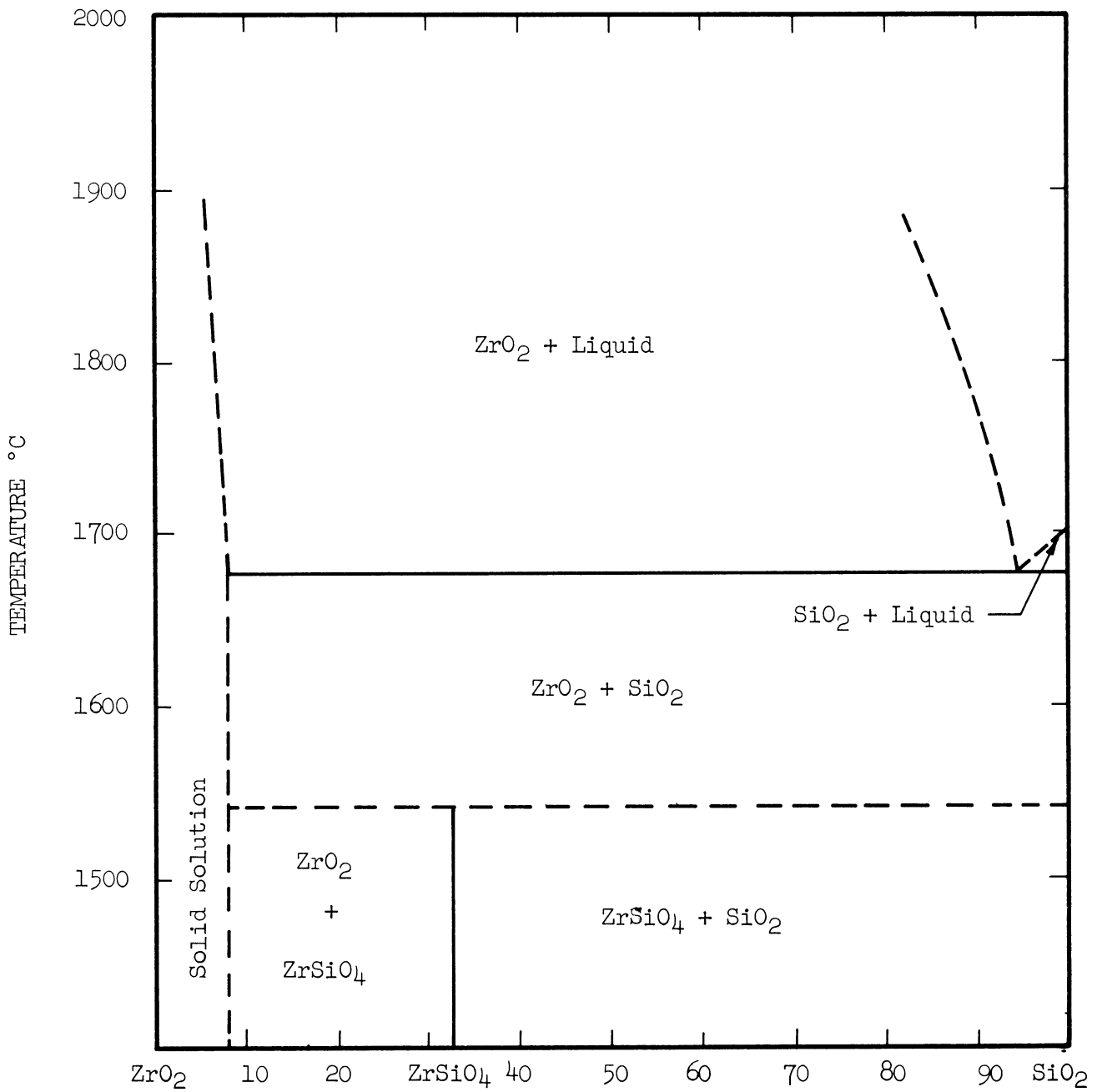


Figure 14. Constitution Diagram of the ZrO<sub>2</sub>-SiO<sub>2</sub> System from C. E. Curtis, H. G. Sowman.

Jour. Am. Ceram. Soc., 36, 6198 (1953).

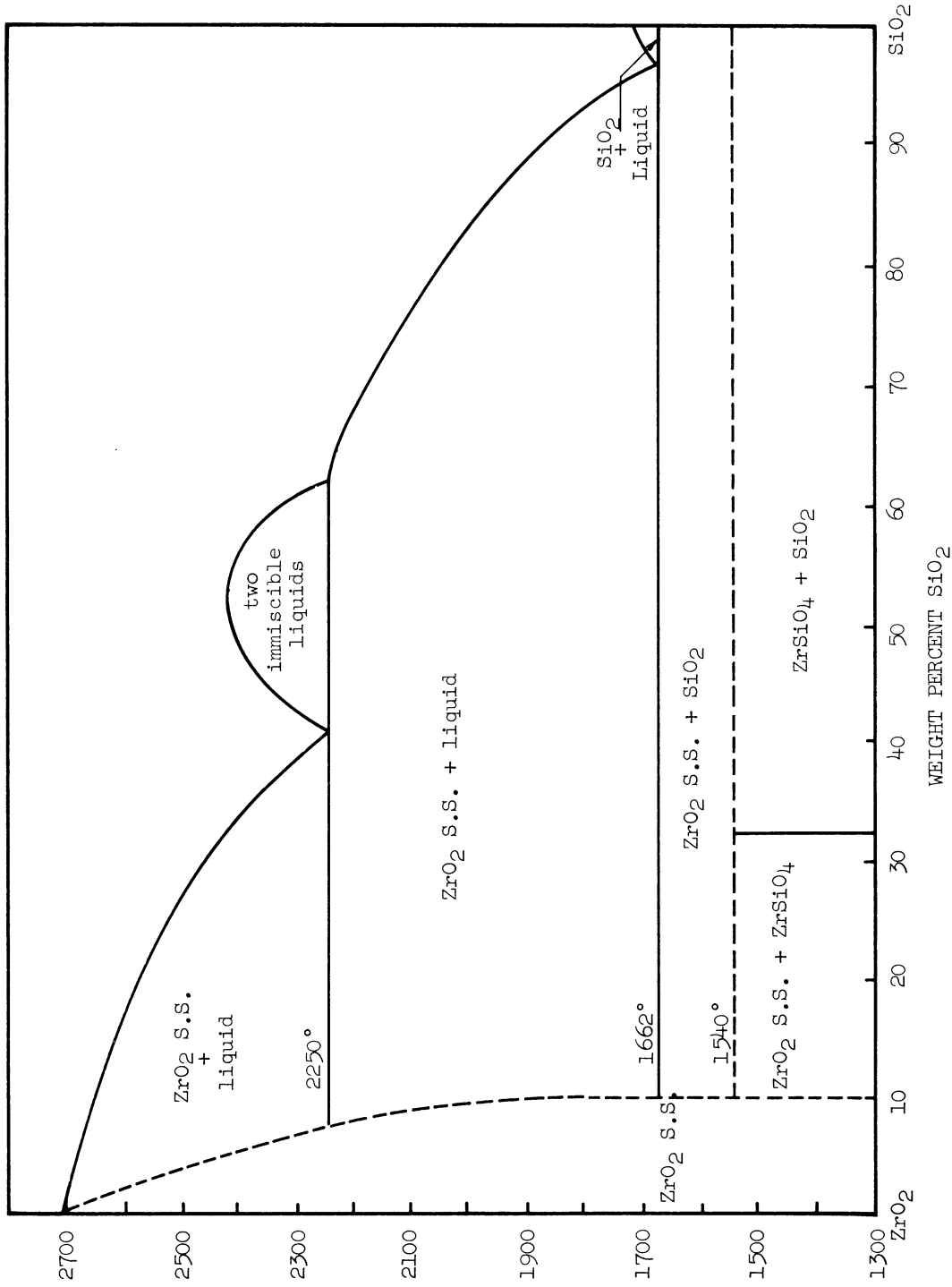


Figure 15. The System ZrO<sub>2</sub>-SiO<sub>2</sub> according to N. A. Toropov and F. J. Galakov, Izvestia.

Akad. Nauk. SSSR, Otdel. Khim. Nauk. No. 2, 160 (1956).

reported a two liquid region but did not attempt to define the limits. The present study confirms the dissociation of zircon to  $ZrO_2$  and silica at temperatures above  $1550^\circ C$ . An attempt to find the two phase region by melting the proper compositions in an oxy-gas flame and quenching in a stream of water was unsuccessful although the two liquid regions in the  $FeO-SiO_2$  and the  $MgO-SiO_2$  systems could be observed by this method.

In the ternary system, the join between zirconia and fayalite is a binary system. This system has not been previously reported in the literature. In this study it was found to have a eutectic at about 4 percent  $ZrO_2$  and at  $1182 \pm 4^\circ C$ . Because the melting temperature of the iron crucibles is about  $1530^\circ C$ , the liquidus surface above  $1500^\circ C$  was not determined. This system was investigated by quenching experiments as described above. The compositions which were studied are shown in Figure 16. An illustration of the appearance of the microstructure in samples quenched from below the eutectic and from above the eutectic is given in Figure 17-A and 17-B. In 17-A the phases present are essentially those of the mixed and pressed specimen with some solid state sintering possible. In 17-B, the primary crystals of zirconia and the eutectic of fayalite and zirconia are evident. By this method the eutectic temperature was determined to be  $1182 \pm 4^\circ C$ . Figures 17-C and 17-D also show the primary crystals of zirconia at 5 percent and 10 percent of  $ZrO_2$ . At 2.5 percent of  $ZrO_2$  only the

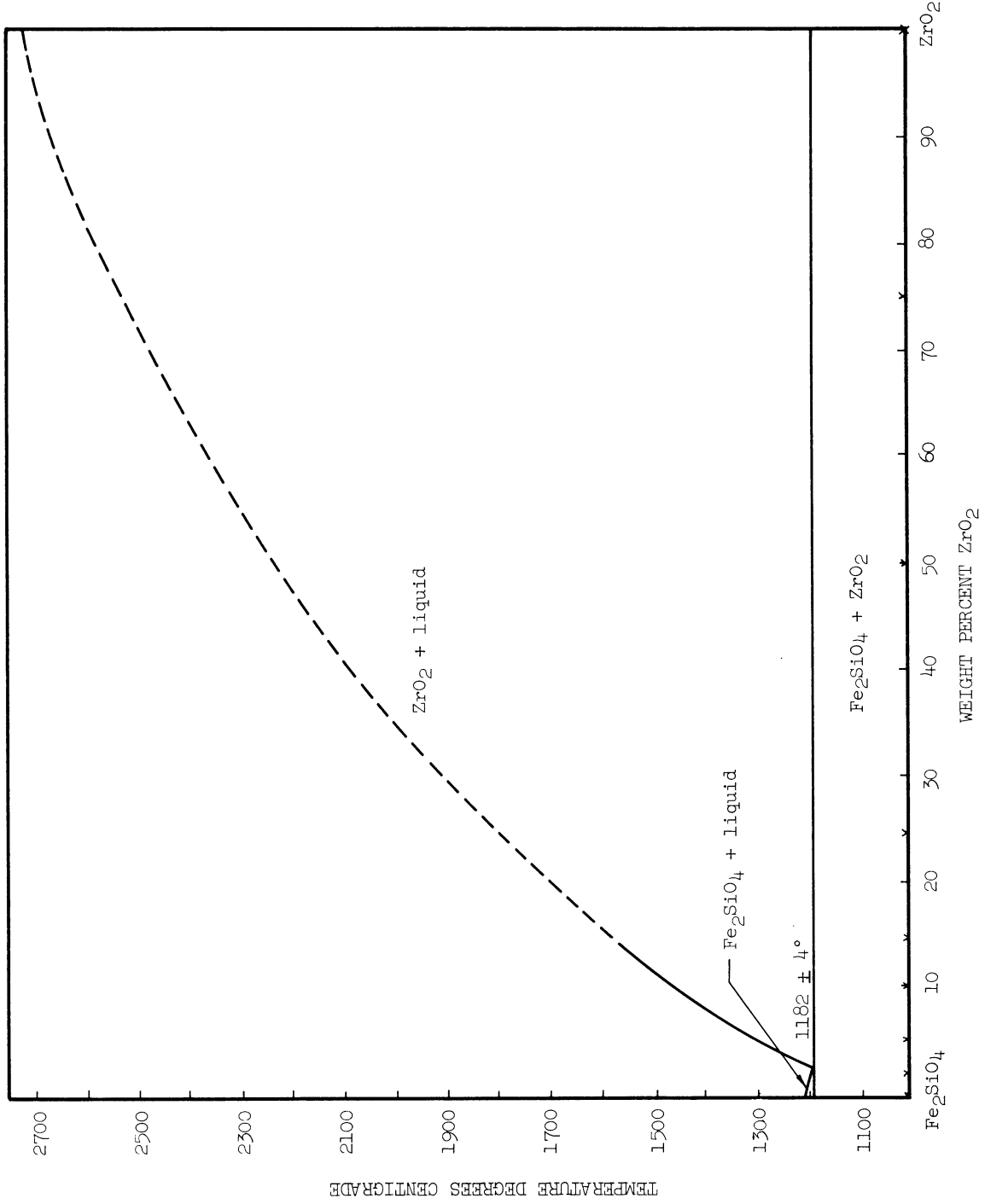
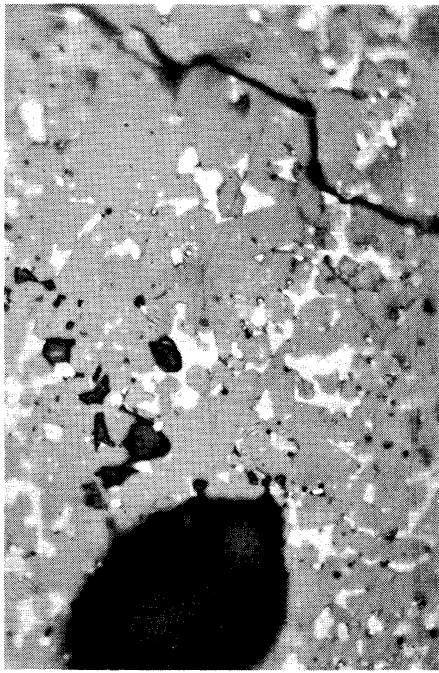
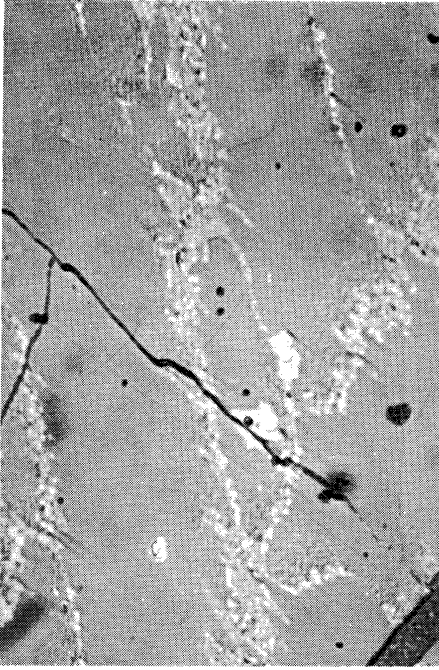


Figure 16. The System Fayalite - Zirconia (x's indicate compositions studied).



A. Mix 31, 1175°C, 15 min, water quenched.



B. Mix 31, 1250°C, 3 min, water quenched.



C. Mix 31, 1250°C, 5 min, then cooled to 1150°C, 15 min, water quench.



D. Mix 30, 1250°C, 5 min, then cooled to 1150°C, 15 min, water quench.

Figure 17. Photomicrographs of Compositions in  
Fayalite-Baddeleyite System. 500X

eutectic structure and a glassy phase were observed. It was, therefore, concluded that the eutectic is between 2.5 percent and 5 percent of  $ZrO_2$ .

### Ternary Invariant Points

In the compatibility triangle  $FeO-ZrO-Fe_2SiO_4$ , the ternary eutectic lies at approximately: 71%  $FeO$ , 7%  $ZrO_2$ , and 22%  $SiO_2$ . The eutectic temperature is  $1157 \pm 4^\circ C$ . In the other compatibility triangle,  $ZrO_2-SiO_2-Fe_2SiO_4$  the ternary eutectic lies at approximately: 58%  $FeO$ , 4%  $ZrO_2$ , and 38%  $SiO_2$ , and at a temperature of  $1166 \pm 4^\circ C$ . The latter triangle also contains a ternary peritectic as the result of the dissociation of zircon. That is, zircon has a field of primary crystallization which does not include the zircon composition. The peritectic temperature is reported by Curtis and Sowman to be about  $1530^\circ C$ . The present work has shown nothing that would be contrary to this. Figure 18 shows the invariant points in the system.

The method for determining the ternary eutectic points was essentially the same as that described for the binary system. In the ternary system the primary field of crystallization may be established. The approximate distance from the boundary line where the second phase begins the crystallization may be determined in the microsection by observing the distribution and amounts of the phase present. For example in establishing the position of the eutectic in the composition triangle  $FeO-ZrO_2-Fe_2SiO_4$ , microsections of the mixes 32, 33, and 49 were examined after quenching

from 1225°C. In mix 32 the primary phase was observed to be zirconia with wustite as the second phase to precipitate. All of the fayalite is in the eutectic precipitate. The situation in mix 33 is somewhat different for here wustite is the primary phase with fayalite as the second phase and baddeleyite only in the eutectic. Mix 49 again shows a different sequence, with fayalite as the primary phase, wustite as the second phase, and baddeleyite only in the eutectic precipitate. By constructing lines through the mix compositions along the paths of crystallization, as indicated by the microstructure, the eutectic can be located to within a small area. The same procedure was followed in the system  $ZrO_2$ - $Fe_2SiO_4$ - $SiO_2$  with mixes 35, 53, and 58, with the results as reported in the preceding paragraph.

#### Primary Crystallization Fields

In the quasi-ternary  $FeO$ - $ZrO_2$ - $SiO_2$  system there are six fields of primary crystallization, namely: wustite, fayalite, tridymite, cristobalite, zircon, tetragonal zirconia. The field of metallic iron also extends into this system. The phase having by far the largest region of primary crystallization is zirconia, which covers well over three-quarters of the area. This is, of course, the result of having all the eutectics in the system at the extreme opposite side from  $ZrO_2$ . The liquidus temperatures in this area are all well above the temperature range in which monoclinic zirconia is stable, and therefore, the zirconia which crystallizes out of the melt is tetragonal. This accounts for the

difference in appearance of the precipitated zirconia from that zirconia which has formed or grown in the solid state.

Because of the defect nature of ferrous oxide, some ferric iron is present. However, it is not present as a separate phase but is present within the wustite structure<sup>(5)</sup>, and maintains electrical balance offsetting the missing ferrous iron positions. The relative concentration of ferric iron in different compositions according to atmosphere and quenching medium is shown in Table IV and Figure 18. Because of the possibility of oxygen pickup during quenching in all samples except those in the sealed iron crucibles, it is probable that the latter more nearly represents the true equilibrium relationship between free iron and ferric oxide in the various compositions at 1200°C. Iron also occurs as a primary phase over an appreciable region around the FeO apex. The FeO-ZrO<sub>2</sub>-SiO<sub>2</sub> system can be considered as ternary only if this iron phase is neglected. The field of primary crystallization of wustite is relatively small, being bounded by lines joining the points at FeO, A, J, and B in Figure 8. The method for determining the eutectic points and the boundary lines was discussed in the previous section. The exact shape of the wustite-zirconia and the wustite-fayalite boundary lines is not known, but they must be close to those shown in order to explain the phase relationships found in the microsections. The fayalite field of primary crystallization, which also contains some free iron, is even smaller than the wustite field. It is depressed somewhat toward the fayalite composition at the fayalite-zirconia eutectic point. In the binary system ZrO<sub>2</sub>-SiO<sub>2</sub> the phase zircon



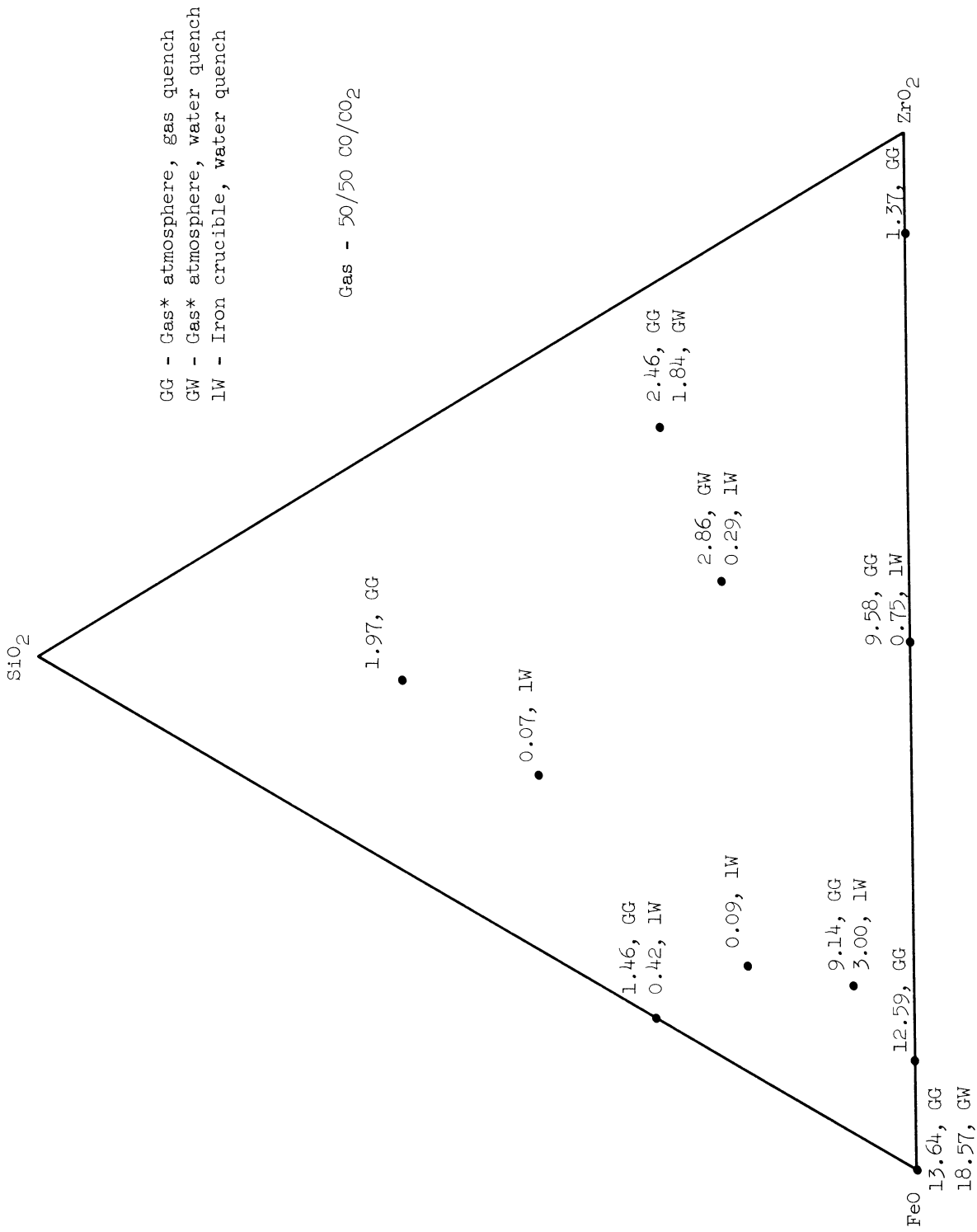


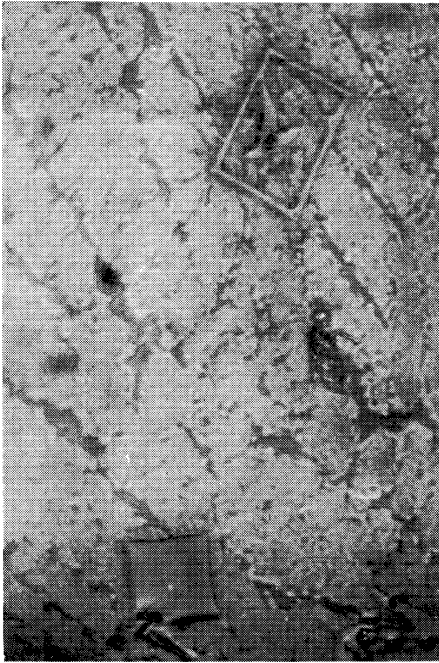
Figure 18. Iron Content of Samples Fired at 1200°C.

on heating dissociates in the solid state below the eutectic and therefore does not crystallize out of a melt. However, in this ternary system a field of primary crystallization of zircon does exist (Figure 19-A). This field appears to be associated with the 1500°C isotherm. It is the field which was least well defined in the present study.

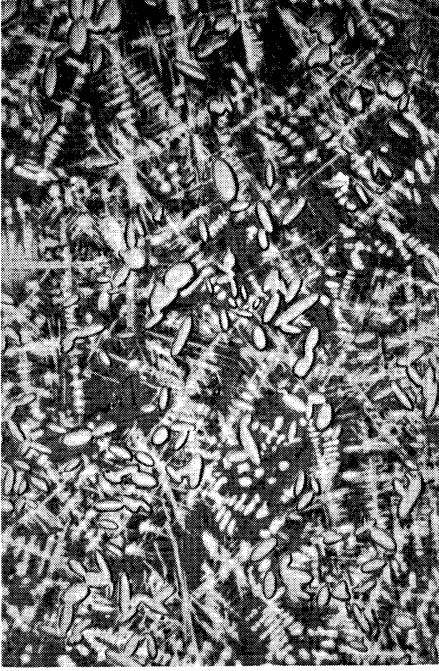
Figure 19-B illustrates the necessity of sealing the crucible in an inert atmosphere. In 19-A the iron plug was inserted in a purified argon atmosphere then the plug was welded in. In 19-B the plug was inserted in air and was not welded. It may be observed that the system has moved down into the ternary region containing baddeleyite as the result of the formation of ferrous oxide from the small amount of entrapped air.

#### Effect of HfO<sub>2</sub> and other Impurities on ZrO<sub>2</sub> Transformation

A number of authors have pointed out that the monoclinic-tetragonal transformation on heating ZrO<sub>2</sub> takes place over a range of temperatures rather than at a single temperature. It has also been noted that the reverse transformation on cooling takes place at lower temperatures than that on heating. This information as well as that of the present study is shown in Table V. Since all of the ZrO<sub>2</sub> available until recently has contained from 1.5 to 4 percent by weight, or more, of hafnium, and since hafnia has been found to transform at temperatures about 500°C higher than zirconia, it seemed reasonable to suppose that



A. 625X



B. 500X

Figure 19. Mix 17, Effects of Loading Technique.

A, Sealed in purified Argon, top welded, heated at 1500°C for 30 minutes, air quenched, shows primary Zircon crystals in matrix of Zircon-Fayalite eutectic and glass; B, sealed in air, top not welded, heated at 1200°C for 30 hours, quenched in water, shows Baddeleyite, Wustite, Fayalite, and Glass.

the presence of hafnium may have some effect upon the transformation of zirconia.

Curtis, Donney and Johnson<sup>(22)</sup> have investigated the effects of hafnia upon the lattice parameter of zirconia by means of X-rays. The same authors checked on heating the monoclinic-tetragonal transformation of zirconia containing only 80 ppm of hafnia by means of DTA. Mumpton<sup>(36)</sup> also checked the transformation by DTA on heating and on cooling. The zirconia used by Mumpton was reported to contain less than 300 ppm of hafnia but other impurities such as  $\text{TiO}_2$  were not listed. Curtis, et al, found an endothermic peak starting at about  $1100^\circ\text{C}$  reaching a maximum at  $1190^\circ\text{C}$  and ending at  $1250^\circ\text{C}$ . They did not report the results on cooling. Mumpton found an endothermic peak beginning at about  $1170^\circ\text{C}$ , reaching a peak at  $1190^\circ\text{C}$  and ending at  $1230^\circ\text{C}$  on heating. On cooling the exothermic peak began at  $1040^\circ\text{C}$ , reached a maximum at  $1015^\circ\text{C}$  and ended at  $980^\circ\text{C}$ . In the present investigation, with zirconia containing less than 500 ppm of hafnia and total impurities less than 0.25 percent, on heating an endothermic peak was found to begin at  $1170^\circ\text{C}$ , reach a maximum at  $1199^\circ\text{C}$  and reach completion at  $1230^\circ\text{C}$ . These temperatures are averages of four runs. On cooling the peak was found to begin at  $908^\circ\text{C}$ , reach a maximum at  $880^\circ\text{C}$  and end at  $850^\circ\text{C}$ . This is a difference of about  $135^\circ\text{C}$  lower than Mumpton's data. However, it is interesting to note that when 10 percent of  $\text{HfO}_2$  is added to the "pure" zirconia, fired for 4 hours at  $1650^\circ\text{C}$  and a DTA is run, the peak on cooling is very near that

reported by Mumpton. The same is true when 5 percent of silica is added to the pure zirconia, fired for 4 hours at 1500°C and a DTA determination is made. Figure 20 shows schematically these DTA results as compared with that reported by Mumpton.

Qualitatively the above results may be explained either from the standpoint of free energy relationships or that of solid state reaction kinetics. If we assume first that Mumpton's material contained sufficient impurities other than hafnia to have an effect upon the transformation temperature the data begin to fall into a certain pattern. It is, of course, very probable that the "true" transformation temperature lies someplace between the transformation which takes place on heating and that which takes place on cooling. The difference in free energy between the "true" transformation temperature and the actual temperature would correspond to the driving force necessary for the nucleation and growth of the new phase. In the "pure" material the temperature difference would be about 160°C which would correspond an activation energy of X. In the impure materials the "true" transformation temperature would probably be from 50 to 75 degrees C higher than that of the "pure" material on the basis of the DTA data. The free energy difference representing the driving force would in turn be considerably less. This would correspond to a different activation energy Y perhaps one-half that of X. This could be interpreted on the basis that the impurities act as nucleation agents thereby lowering the

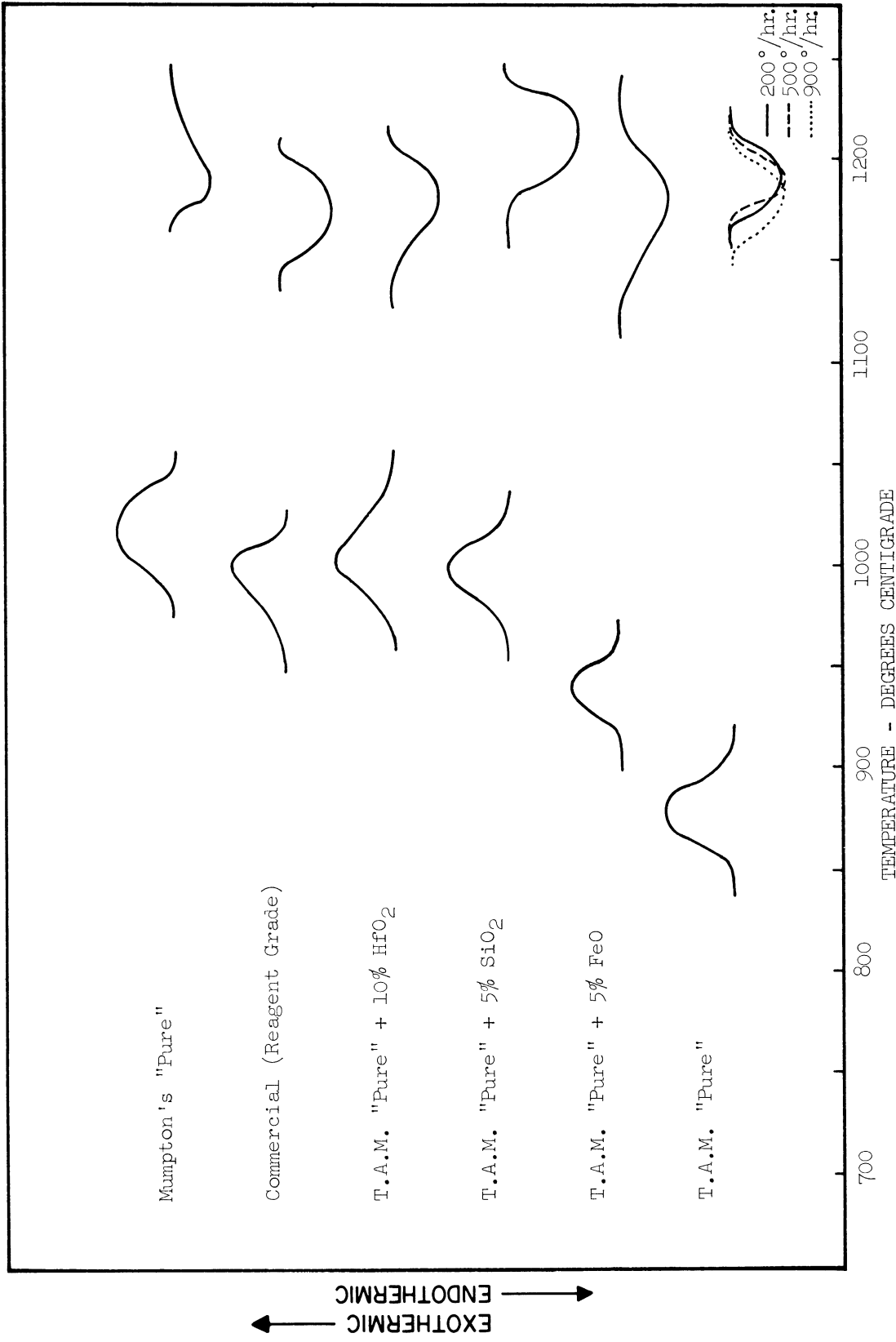


Figure 20. Effects of Impurities on Zirconia Phase Transformations, DTA Curves, Endothermic on Heating, Exothermic on Cooling.

energy required for the formation of the new phase (Figure 21). This, of course, does not rule out the possibility of kinetic effects. However, two other bits of information make the kinetic concept less attractive. First, Table VI shows essentially no effect of heating rate upon the transformation of monoclinic to tetragonal zirconia as determined by differential thermal analysis. Second, Mumpton found that upon heating  $ZrO_2$  to above the transformation temperature then cooling to below that temperature and just above the lower "cooling" transformation temperature baddeleyite lines were not found even after 12 hours holding time, only the tetragonal lines were found.

The differential thermal analysis work of the present investigation was supplemented by high-temperature X-ray diffraction and excellent correlation was obtained on the phase transformation temperatures by the two methods. In the high-temperature X-ray work the (111) peak of the tetragonal phase and the (111) and ( $1\bar{1}1$ ) peaks of the monoclinic (baddeleyite) phase were used for identification. The high-temperature X-ray camera used was similar to that described by Van Valkenburg and H. F. McMurdie<sup>(36)</sup>.

#### Dissociation of Zircon

It has been realized for some time that zircon dissociates into zirconia and silica at elevated-temperatures. Matignon<sup>(38)</sup> observed that zircon dissociates into zirconia and silica at 1800°C and above. Barlett<sup>(35)</sup> found that a quenched melt of zircon had decomposed into  $ZrO_2$  and a high

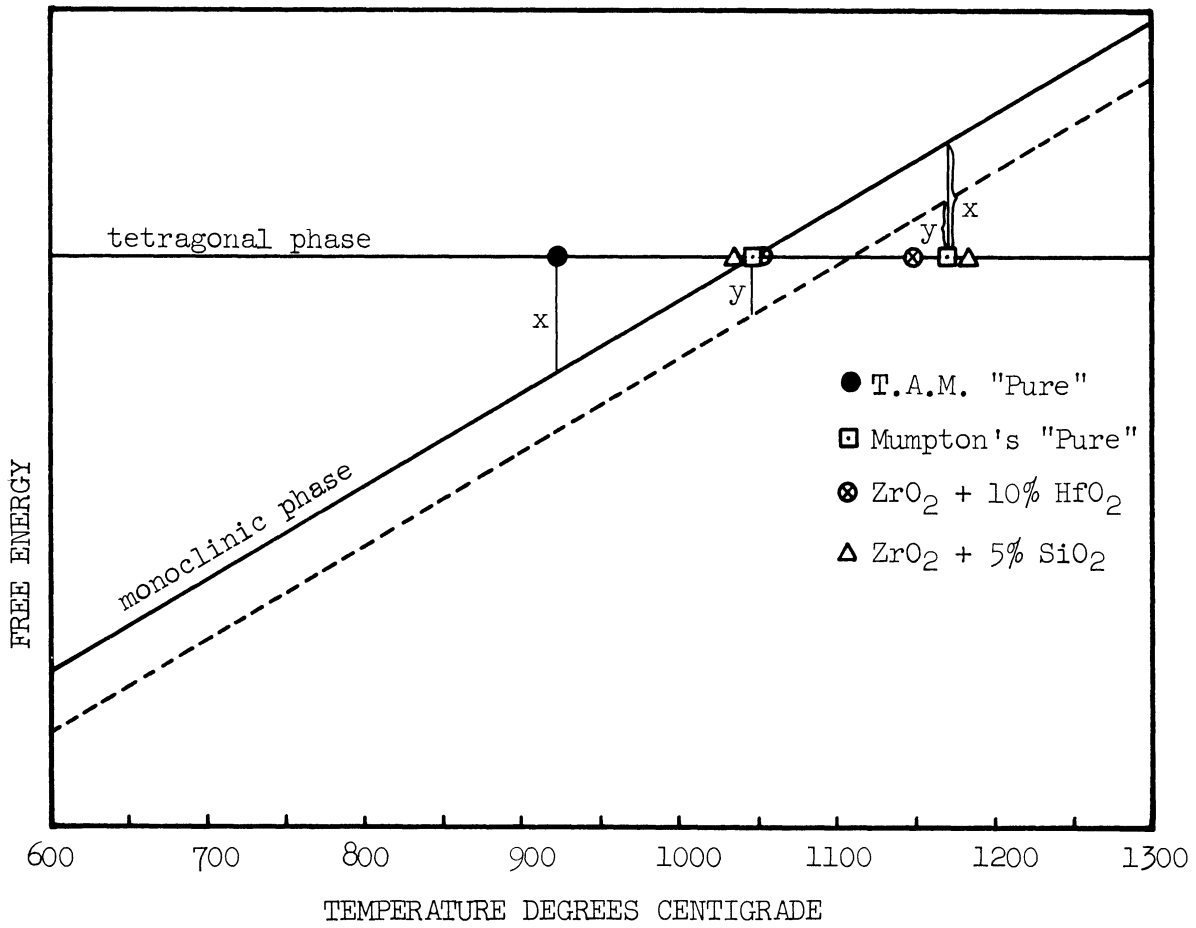


Figure 21. Schematic Free Energy versus Temperature of Beginning of Transformation for  $ZrO_2$ .



Table I

Semi-Quantitative Spectrographic Analyses of Raw Materials Used

(They are reported as oxides of the elements indicated.)

Oxide	TAM ZrO <sub>2</sub>	FISHER ZrO <sub>2</sub>	ZIRCON FLOUR	AUSTRALIAN ZIRCON	SILICA FLOUR
Mg	.003%	.04%	.003%	.001%	.01%
Al	.001	.02	.2	.003	.01
Si	.02	.5	high	high	high
Ca	.003	.03	.005	.003	.003
Ti	.015	.2	.4	.3	.005
Cr	.008	.003	.003	.003	.003
Fe	.05	.02	.04	.01	.01
Ni	.003	.01	.006	.005	.007
Cu	.001	.001	.001	.001	.003
Sr	.001	.008	.001	.001	.004
Zr	high	high	high	high	.005
Ba	.004	.05	.003	.003	.0005
Pb	.008	.01	.008	.008	.008
Sc	.002	.002	.005	.003	
Y	.005	.005	.3	.15	
Yb	.002	.002	.05	.02	
Hf	<.05	4.	2.	1.5	

Table II

Analysis of Ferrovac "E" 3/8-in. Rod  
used for Crucibles and Lids

Element	Wt. Percent
C	0.025
Mn	0.005 or less
Si	0.007
Ni	0.005
O	0.0023
N	0.0004
P	<0.01
S	<0.01
Mo	<0.01
Cr	<0.01
V	<0.01
Sn	<0.01
Al	<0.01
Co	<0.01
Cu	<0.01
Pb	<0.01

Table III

Results of Quenching Experiments, 1020 Steel Specimen  
 3/8" Square by 3/4" Long, with Thermocouple Sealed  
 in Center: Temperatures in Degrees Centigrade

Quenching Medium	0 sec.	1 sec.	2 sec.	3 sec.	4 sec.	5 sec.	10 sec.	15 sec.	20 sec.
Water	1065	1000	760	38	-	-	-	-	-
Water	1095	1060	815	590	65	-	-	-	-
Water	1110	1040	870	540	260	65	-	-	-
Dibutyl Phthalate	1095	1040	970	855	730	605	290	205	160
Dibutyl Phthalate	1095	1010	900	815	705	605	290	205	155
Dibutyl Phthalate	1065	980	900	815	705	620	290	205	120
Mercury Spec. Floating	1095	1010	905	800	755	680	480	280	205
Mercury Spec. Floating	1040	980	900	820	775	730	565	410	315
Mercury Spec. Submerged	1120	1065	955	875	815	745	540	300	175
Mercury Spec. Submerged	1095	1045	915	800	720	650	455	250	150

Table IV

Comparison of Ferrous and Ferric Oxide Content of some Specimens Fired in an Atmosphere of 50/50 CO/CO<sub>2</sub> with those Fired in Iron Crucibles

Specimen No.	Environment	Quenching Medium	Fe <sup>++</sup>	Fe <sup>+++</sup>	Total Fe
1	Gas	Gas	62.09	13.64	75.73
1	Gas	Water	56.10	18.57	74.67
2	Gas	Gas	48.66	9.14	57.80
3	Gas	Water	19.37	2.86	22.23
4	Gas	Gas	8.20	2.46	10.66
4	Gas	Water	9.28	1.84	11.12
6	Gas	Gas	50.84	1.46	52.30
7	Gas	Gas	9.48	1.97	11.45
10	Gas	Gas	6.52	1.37	7.89
11	Gas	Gas	28.51	9.58	38.09
12	Gas	Gas	45.38	14.59	59.97
2	Iron	Water	58.21	3.00	61.21
3	Iron	Water	19.26	0.29	19.55
6	Iron	Water	54.09	0.42	54.51
11	Iron	Water	36.67	0.75	37.42
21	Iron	Water	31.65	0.07	31.72
32	Iron	Water	54.64	0.09	54.73

Table V

DTA Data on Zirconia Monoclinic-Tetragonal Transformations

Source	Heating			Cooling		
	Begin	Peak	End	Begin	Peak	End
Curtis et al.	1100	1190	1250	-	-	-
Mumpton	1170	1190	1230	1040	1015	980
Allison & Taylor				987		
Bunting	1170			1034		
Present "Pure"	1162	1187	1213	908	880	850
Present (10% HfO <sub>2</sub> )	1136	1185	1207	1046	1002	967
Present (.5% SiO <sub>2</sub> )	1176	1215	1244	1012	992	973
Present (5% FeO)	1125	1187	-	959	941	915
Present (4% HfO <sub>2</sub> Commercial)	1141	1177	1215	1014	990	955

Table VI

Effect of Heating Rate upon ZrO<sub>2</sub> Transformation

Heating Rate	Peak	Begin	End
200°/hour	1192	1165	1217
500°/hour	1185	1170	1212
900°/hour	1184	1150	1209

silica glass. Geller and Lang<sup>(30)</sup> in a phase diagram of the system  $\text{SiO}_2\text{-ZrO}_2$  show a dissociation of zircon into zirconia and a liquid at  $1775^\circ\text{C}$ . Curtis and Sowman<sup>(31)</sup> found zircon to dissociate in the solid state into zirconia and silica at about  $1540^\circ\text{C}$ . Mumpton<sup>(36)</sup> also found the dissociation to take place in the solid state someplace between  $1500^\circ\text{C}$  and  $1600^\circ\text{C}$ . The present investigation has shown that zirconia and silica intimately mixed will combine to form zircon at temperatures up to  $1500^\circ\text{C}$  while zircon fired for 4 hours at  $1600^\circ\text{C}$  shows zirconia lines when X-rayed, indicating that dissociation has occurred. No evidence of a melt could be found microscopically in the zircon fired at  $1600^\circ\text{C}$ .

#### Immiscible Liquid Regions

In the system  $\text{FeO-SiO}_2$  a region of two immiscible liquids extending from 96.9 percent  $\text{SiO}_2$  to 55.3 percent  $\text{SiO}_2$  at a temperature of  $1690^\circ\text{C}$  was reported by Greig<sup>(39,40)</sup>. Further work in ferrous oxide-silica systems has been in general agreement with Greig's work. In the system  $\text{ZrO}_2\text{-SiO}_2$  Barlett<sup>(35)</sup> reported that when melted, a mix of 50 percent  $\text{ZrO}_2$  and 50 percent  $\text{SiO}_2$  forms two immiscible liquids, one of which devitrifies upon cooling. Barlett did not attempt to define the composition nor temperature of the immiscible liquids region. Toropov and Galakov<sup>(32)</sup> investigated the system  $\text{ZrO}_2\text{-SiO}_2$  at temperatures above  $1800^\circ\text{C}$  supplementing the work of Curtis and Sowman<sup>(31)</sup> who investigated the system below  $1800^\circ\text{C}$ . The Russian authors report a region of liquid immiscibility in the system from

41 to 62 weight percent of silica at 2250°C, extending to a maximum at 53 percent silica and 2430°C. In melts in the two liquid region they find a clear highly siliceous liquid containing spheres of a second liquid which upon cooling becomes turbid due to the very fine precipitate of zirconia.

Barlett<sup>(35)</sup> melted the mixes in a carbon arc and allowed the liquid droplets to fall into a trough of running water. Toropov and Galakov<sup>(32)</sup> melted small samples of the mixes in a 5 mm spiral of tungsten wire in an oxygen-free argon atmosphere.

The present work checking compositions in the binary regions (FeO-SiO<sub>2</sub> and ZrO<sub>2</sub>-SiO<sub>2</sub>) and in the ternary region ZrO<sub>2</sub>-FeO-SiO<sub>2</sub> was accomplished by melting small plugs 1/8" in diameter by 1/8" high in an oxy-acetylene flame and quenching the melt with a water spray. Some compositions were also mixed with a small amount of Duco cement and formed into fibers 1 mm or less in diameter and two or three centimeters long. These fibers were melted in an oxy-acetylene flame and the molten ends allowed to drop into a beaker of water. Melts of FeO and SiO<sub>2</sub> and of MgO and SiO<sub>2</sub> in the proper proportions made by the former process showed clearly the two liquid characters. However, because of the rapid devitrification of one liquid in the ZrO-SiO<sub>2</sub> system, the results were not quite so clear cut.

#### Effects of Ferrous Oxide on Zircon and Zirconia Refractories

Probably the most important result of this study, as far as

refractories is concerned, is that wustite and zircon are not compatible. As a result of this incompatibility zircon will dissociate to form an iron-rich silicate liquid or fayalite and baddeleyite when in contact with a slag containing free ferrous oxide. This may occur even at temperatures below 1200°C. The amount of liquid formed at any particular ferrous oxide level will not be greatly different from that which forms when ferrous oxide comes in contact with a silica brick. However, the effect of the liquid will not necessarily be the same for the two different refractories. The surface tension of the liquid in contact with the refractory grains and the degree of solid-to-solid contact between the grains play an important role in the behavior of the refractory in service<sup>(40,41)</sup>. In the references cited, the authors compare the role of the liquid phase in periclase refractories as compared with silica refractories. It is shown that with the large degree of solid-to-solid contact in the silica refractory that there is considerable strength under load even with 25 percent of liquid present. With less than 5 percent of liquid in periclase refractories failure can occur through spalling and peeling. This results chiefly from the small degree of surface contact between the nearly spherical periclase grains. The lower viscosity of the magnesia-iron silicate liquid and a probably lower surface tension of liquid in contact with the periclase grains no doubt have an additional important effect on this high temperature weakness. The present investigation would indicate that zircon too would be expected to be relatively weak at



high temperatures in the presence of ferrous oxide because here, too, a fluid slag is formed which penetrates easily between the grains causing partial or total dissociation of the zircon. The zirconia resulting from this reaction is in the form of rounded "rice grain" particles which have little solid to solid contact. This may be seen in Figure 19-B.

In zirconia refractories the effect of ferrous oxide would not be expected to be so severe as with zircon. Ferrous oxide and zirconia are compatible, and the temperature at which the first liquid is formed is over 150 degrees centigrade above that at which it is formed in the zircon refractory. The microstructure of zirconia would indicate that it should be a more refractory material at high temperatures than at intermediate temperatures. The reason for this is that at intermediate temperatures zirconia tends to be rounded, similar to periclase, and the ferrous oxide liquid penetrates easily between the rounded grains (Figure 12). At higher temperatures this liquid could aid in the sintering of these grains to form a network somewhat similar to that in a silica brick. Of course, zirconia has one drawback which overcomes all of its other desirable characterizations. The transformation from monoclinic to tetragonal phase is accompanied by a change of volume of several percent. In practice this is overcome by adding calcium oxide to the zirconia to form a cubic phase which does not transform and which has more desirable thermal expansion characteristics. The effect of ferrous oxide upon this cubic phase is outside the scope of the present investigation and was therefore not studied.

## SUMMARY

It has been shown that in the quasi-ternary system FeO-ZrO<sub>2</sub>-SiO<sub>2</sub> there are no ternary compounds. Above about 1550°C there are two compatibility regions FeO-Fe<sub>2</sub>SiO<sub>4</sub>-ZrO<sub>2</sub> and FeO-Fe<sub>2</sub>SiO<sub>4</sub>-SiO<sub>2</sub>. Below 1550°C there are three compatibility regions FeO-Fe<sub>2</sub>SiO<sub>4</sub>-ZrO<sub>2</sub>, Fe<sub>2</sub>SiO<sub>4</sub>-ZrSiO<sub>4</sub>-ZrO<sub>2</sub>, and Fe<sub>2</sub>SiO<sub>4</sub>-ZrSiO<sub>4</sub>-SiO<sub>2</sub>. Fayalite and zirconia are compatible and form a binary system. Zircon dissociates at about 1550°C to ZrO<sub>2</sub> and SiO<sub>2</sub>, and therefore the zircon-fayalite system is not a binary system at all temperatures.

The binary system FeO-ZrO<sub>2</sub> has been re-examined and the eutectic temperature located at 1323 ± 3°C. The reported solubility of four percent of FeO in ZrO<sub>2</sub> at 1450°C was disproved. A re-examination of the SiO<sub>2</sub>-ZrO<sub>2</sub> system upheld the work of Curtis and Sowman. In the system fayalite-zirconia a eutectic was found at four percent ZrO<sub>2</sub> and 1182 ± 4°C.

Two ternary invariant points were located. In the FeO-ZrO<sub>2</sub>-Fe<sub>2</sub>SiO<sub>4</sub> region a ternary eutectic lies at approximately 71 per cent FeO, seven per cent ZrO<sub>2</sub>, and 27 percent SiO<sub>2</sub> and at 1157 ± 4°C. In the ZrO<sub>2</sub>-SiO<sub>2</sub>-Fe<sub>2</sub>SiO<sub>4</sub> region a ternary eutectic lies at approximately 58 percent FeO, four percent ZrO<sub>2</sub>, and 38 percent SiO<sub>2</sub> at a temperature of 1166 ± 4°C. There is a small field of primary crystallization of zircon and a ternary peritectic in the system also.

Six fields of primary crystallization were observed: wustite, fayalite, tridymite, cristobalite, zircon, and tetragonal zirconia.

The field of metallic iron also extends into this system making it a quasi-ternary system.

The presence of  $\text{HfO}_2$  and other impurities were shown to have a decided effect upon the monoclinic-tetragonal transformation of zirconia. The chief effect was that of closing the hysteresis between the transformation temperature on heating and that on cooling.

The region of liquid immiscibility reported by Toropov and Galakov in the system  $\text{SiO}_2\text{-ZrO}_2$  could not be reproduced, but was not definitely disproved by this work.

The most important result of this study to a refractories application is that wustite and zircon are not compatible. As a result of this incompatibility relatively small amounts of wustite will cause a dissociation of zircon to form an iron rich silicate liquid or fayalite and baddeleyite at temperatures as low as 1200C.

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