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THE USE OF CARBIDES IN REFRACTORIES

BY

JAMES A. CROOKSTON

A

THESIS

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Approved by Paul G. Herold
Professor of Ceramic Engineering

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INTRODUCTION

Demands are being made on the ceramic industry by other industries for better refractories and refractory articles to withstand higher temperatures and more rigorous treatment in practice. One industry where this is especially true is the aircraft industry. With the advent of jet propelled planes and rockets, the limitations of metals for certain uses became apparent. With the failure of metals because of the rigorous treatment they received, ceramics was turned to as a possible solution. The use of ceramics for certain parts proved to be very satisfactory. Ceramic parts are now being used for those areas on aircraft where high temperatures are attained in a very short period of time. Special refractories are needed to withstand the high temperature and the great heat shock. Another place where ceramics is being used in the aircraft industry is in the gas turbines, where ceramic blades are now being used. Originally, ceramic coatings on metal blades were used, but at present efforts are being made to make the blades entirely of ceramic materials. For this use, the ceramic parts must have high mechanical strength to withstand the strain when the gas turbine is in use. They must also have a high thermal shock resistance and high refractoriness. With the successes attained with ceramics in the aircraft industry thus far, there will undoubtedly be an effort made to make further use of ceramics in this industry. By using ceramic parts it is possible to use higher operating temperatures with a resultant power increase, and the total weight is decreased, again adding to the available power.

With the new demands being made on the ceramic industry in mind, it was thought that an investigation of the ceramic possibilities of certain high melting refractory materials might prove of interest and value. The high melting materials are the oxides, carbides, nitrides, borides, and hydrides. Since a great deal of work has been done on the oxides, and relatively little on the others, the oxides were dismissed. Of the other groups, the carbides seemed interesting. Of the carbides, the following materials were chosen for investigation: Boron Carbide (B_4C), Zirconium Carbide (ZrC), and Titanium Carbide (TiC). These materials were chosen because of their high melting points, apparent stability at high temperatures, and the fact that authorities on refractories suggested that they might have good possibilities.

REVIEW OF LITERATURE

In reviewing the literature on the carbides selected for investigation, it was seen that little work has been reported on these materials regarding their use in ceramics or refractories. In order to determine a suitable method of investigating the possibilities of other carbides in refractories, and also to show what benefits might result from their use in refractories, a review of the literature on SiC was made.

A compilation of information on SiC refractories by A. C. Lea[1] gives a good deal of information regarding these refractories.

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[1] Lea, A. C., Silicon Carbide and Its Use as a Refractory Material, Trans. Brit. Cer. Soc., Vol. 40 (4), pp. 93-118 (1941).

According to him, three methods are used in producing SiC refractory bricks: (1) Exposure of the shape made of carbon to silicon vapor at a high temperature. (2) Shaping the article from SiC without any permanent bonding material and heating it to a temperature near the formation temperature of SiC. This is in essence a recrystallization of the SiC. (3) By bonding the SiC grains with a material that can be vitrified on heating.

Various materials have been suggested as bonds for the third method, such as: iron, iron oxide, or salts of iron; sodium silicate, clay, borax, boric acid, lime, Portland cement, aluminum sulphate, magnesite, dolomite, and zirconium and aluminum silicate. At the present time the majority of bonded SiC refractories use a refractory clay as the major constituent of the bond. The methods of making the bonded refractory are: hand molding from a plastic mixture, machine pressing, and hand ramming. The firing is carried to a maximum of 1400°C. with care being taken to avoid an excess of oxygen at certain temperatures. According to H. N. Baumann and J. P. Seventzel[2], SiC refractories are now nearly always protected by a refractory type of glaze, to reduce the possibility of oxidation of the SiC grains.

There is some controversy as to when the oxidation of SiC begins, when it stops, and how great it is. L. E. Muller and L. H. Baraduc[3]

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[2] Baumann, H. N. and Seventzel, J. P., Physical Properties of SiC Refractories, Bull. Am. Cer. Soc., Vol. 16, p. 419 (1937).

[3] Muller, L. E. and Baraduc, L. H., Rev. Met., Vol. 6, p. 700 (1909).

say that SiC is not oxidized at 1000°C. in oxygen, at 1000°- 1350°C. it is slightly oxidized in air, while at 1350°-1500°C. the silica formed fuses. From 1500°-1600°C. the silica fused retards oxidation, while above 1750°C. oxidation is very rapid. F. H. Riddle and A. B. Peck[4] found that SiC test pieces run at 600°-1000°C. for 18 months in a tunnel kiln had oxidized and swelled to twice their normal size. F. L. Nobes[5] says that SiC is slowly oxidized between 1000°C. and 1350°C. S. M. Phelps[6] states that oxidation of SiC may begin at 900°C.

The outstanding properties of SiC refractories are their high hot strength, high hot thermal conductivity, and good resistance to spalling. They are reported to be inactive to acid and neutral slags, non-ferrous and grey cast iron, but are attacked by basic slags, low carbon steels, or iron and lead at temperatures of 900°-1400°C.

F. S. Walton and E. L. Haumann[7] made observations on the effect of SiC in clay bodies. Their method involved using a fairly stiff plastic mix, which was thoroughly pugmilled and allowed to stand 24 hours in a warm damp place. Test bars were made and fired to cones 10, 12, and 14. As the SiC content increased the cold and hot modulus of rupture increased. Slag resistance, and thermal conductivity

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[4] Riddle, F. H. and Peck, A. B., An Eighteen Month High Temperature Test on Refractory Test Specimens, J. Amer. Cer. Soc., Vol. 9, p. 1, (1926)

[5] Nobes, F. L., Ind. Chem., Vol. 6, p. 183 (1930)

[6] Phelps, S. M., Amer. Refr. Inst. Bull., No. 57, April (1935)

[7] Walton, S. F. and Haumann, E. L., Observation on Effect of SiC in Clay Bodies, J. Amer. Cer. Soc., Vol. 13, pp. 935-940, (1940)

increased also as the SiC content increased. Resistance to spalling also showed an increase.

Of the carbides to be investigated, the one which seems to have been investigated most thoroughly is Boron Carbide (B_4C). The crystal structure of B_4C was studied by H. K. Clark and J. L. Hoard[8], and they found that the form B_4C was very stable. In tests made on various forms of Boron Carbide, it was found that if the Boron to Carbon ratio is equal to or greater than 4, the carbide is resistant to attack by either nitric acid or acqua regia, both of which will dissolve Boron. If this ratio is less than 4, graphite can always be detected. From this it seems that the excess Boron goes into solid solution with the Boron Carbide (B_4C) through the accomodation of spaces in the Boron Carbide structure.

A paper by R. R. Ridgway[9] describes the process of manufacture and the physical and chemical properties of Norton's B_4C.

Manufacture: The process is very similar to that for making SiC in that a resistance type of furnace is used because of the graded temperature zones such a furnace contains. These zones allow the carbide to be made from a raw material as boric acid which is volatile and which when reduced gives a metallic compound which is also highly volatile at the reaction temperatures. Due to the vol-

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[8] Clark, H. K. and Hoard, J. L., The Crystal Structure of Boron Carbide, J. Amer. Chem. Soc., Vol. 65, No. 11, pp. 2115-19 (1943)

[9] Ridgway, R. R., Boron Carbide, A New Crystalline Abrasive and Wear-Resisting Product, Trans. Electro Chem. Soc., Vol. 66, pp. 117-133, (1924).

atility the early workers had trouble getting a carbide product free of free graphite, and they also lost a lot of Boron constituent. With the new type of furnace, the Boron losses are low and make the production of B_4C commercially possible.

Boric acid is used in the process and it is first dehydrated to an anhydrous glass. This glass is then placed in a special resistance furnace with a high purity coke, a central heating core is provided, and the surrounding mixture heated to a temperature of around 2500°-2600°C. A cylindrical boron impregnated zone surrounds a zone of freely developed B_4C crystals, inside of which zone there is molten B_4C which forms a thick ingot. This ability to form a molten phase is important and makes possible some of the special applications of Boron Carbide.

Crystallization: From megascopic and microscopic investigations of well crystallized specimens, B_4C has been tentatively placed in the hexagonal system. The most prominent crystal form is the rhombohedron.

Hardness: Boron Carbide is harder than SiC and is between SiC and Diamond in hardness.

Strength: Tests for resistance to compression were made by lapping out small cubes, .3 inches on a side, from a crystal with no flaws and good density. The following tabulation shows the results:

Material	Av. Mod. of Rupt.	Compression	Av. Mod. Rup. in Cross-Bending
Molded B_4C	260,000 lbs/in.^{2}	18,000 Kg/cm^2	44,000 lbs/in.^{2}
Dense SiC	82,000	5,800	
Crystalline Al_2O_3	75,000	5,300	14,000
Quartz Optical	58,000	4,100	
Spark Plug Porcelain	72,000	5,100	
Fused Magnesia	21,000	1,500	
Tungsten Carbide	520,000	37,000	250,000
Tantalum Carbide	267,000	19,000	

Melting Point and Vapor Pressure: B_4C does not seem to have any appreciable vapor pressure at its melting point. The molten B_4C will dissolve Carbon with which it is in contact, this carbon reappearing on cooling as graphite cleavage forms, destroying the strength of the product, its uniformity, and therefore its use as an abrasive. The absorption of Carbon increases the fluidity of the molten phase and changes the melting point. The estimated melting point of pure B_4C is between 2350°C. and 2500°C.

Electrical Conductivity: B_4C is a better electrical conductor than SiC. It exhibits a negative temperature coefficient of resistance. Some values are given below:

TEMPERATURE	OHMS/IN.^{3}	OHMS/CM.^{3}
20°C.	.175	.445
100	.035	.089
200	.016	.041
300	.014	.036
400	.011	.028
500	.009	.023

Coefficient of Expansion: B_4C has the expansion characteristics of SiC as evidenced below:

PRODUCT	TEMP. RANGE	AVER. LINEAR COEFF./°C.
Molded B_4C	25-800°C	45×10^{-7}
Graphite Electrode	20-900	12×10^{-7}
Crystalline Al_2O_3	900°C.	72×10^{-7}
SiC	100-900	47×10^{-7}

Corrosion and Oxidation Resistance: At atmospheric pressure and at 200°C. or below, B_4C is inert to all solutions of acids and alkalies, both concentrated and dilute.

The rate of oxidation of B_4C is about 10 times that for SiC for the powdered form.

A comparison of the oxidation rates of diamond and B_4C is given:

% C Burned to CO_2 in O_2

	DIAMOND			B_4C		
TIME	800°C	900°C	1000°C	800°C	900°C	1000°C
20 Min.	1.3	2.5	99.8	Neg.	.3	.7
40	2.0	3.5	100.0	——	.5	.7
60	2.8	4.5		——	.5	.7
80	3.0	5.5		——	.5	.7

The density of B_4C is around 2.52.

The purposes for which B_4C has been used thus far are as an abrasive and for parts and devices requiring good resistance to abrasion.

A. B. Searle[10] mentions both TiC and ZrC in that he says both are highly refractory and appear to be worthy of attention. He also mentions that TiC crucibles have been made and that they will withstand temperatures of over 2000°C. No mention is made of the conditions under which they are used.

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[10] Searle, A. B., Manufacture and Uses-Refractory Materials, Charles Griffin and Company, Ltd., London, p. 170 (1924)

Mellor[11] gives a summary of work done on TiC. L. Franck found that Ti unites with C in all proportions forming crystalline carbides. H. Moissan obtained TiC by heating TiO_2 with C in an arc furnace for 10 minutes. TiC was also obtained by heating $TiO_2$with CaC_2. The carbide of Ti occurs in fused masses of crystalline fracture or in crystalline aggregates. There is always an excess of C which crystallizes out as graphite.

F. W. Shimer says that TiC is soluble in HNO_3. H. Moissan says TiC is not attacked by HCl, but is slowly attacked by acqua regia. The vapor of H_2O has no action at 600°C. The reactions of the carbide resemble closely those of Ti.

In a paper by W. V. Mikhailov and E. P. Belyakova[12] it is stated that the reduction of TiO_2 by solid C begins at 927°C and the formation of TiC begins at 900°-1000°C. Hydrogen begins to reduce TiO_2 at 900°C. with the maximum effect at 1300°C. Pure TiC was obtained from a mixture of TiO_2 and C after 2 hours at 1850°-1900°C.

Becker[13] states that TiC is easily attacked by N_2 at 1500°C. and up, forming TiN through decarbonization. He gives the unit cell dim-

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[11] Mellor, J., Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. V, pp. 884-5 (1924).

[12] Mikhailov, V. V. and Belyakova, E. P., Investigation of the Reduction of Oxides of Ti in Connection with the Blast Furnace Smelting of High Ti Mixtures, Ural. Metallurg., No. 4-5, pp. 14-19 (1939)

[13] Becker, K., Hochschmelzende Hartstoffe, J. W. Edwards, Ann Arbor, Mich., pp. 49-68, (1935)

ension of TiC as 4.60 A° and the density as 4.25. The hardness is given as being above 8 based on Moh's scale of hardness. The melting point of TiC is given as 3044°-3224°C. TiC has a cubic crystal structure. The specific resistance of TiC in values of Rho .10^{-4} ohm-cm. at room temperature is given as 1.93, while at the temperature of liquid air it is given as 2.94. Thus, at these low temperatures TiC exhibits a negative temperature coefficient of resistance. No resistance figures were given for TiC at the higher temperatures.

Troost[14] heated powdered zircon with carbon in an electric furnace to get metallic-like masses of carbide. His analyses indicated a composition of ZrC_2, but no distinction was made between mixed and combined carbon. This product did not alter in air and was not attacked by water or acids other than HF. If little carbon was used the product did not oxidize in air at red heat, but if much carbon was used to make it, it burned brilliantly.

Moissan[15] on fusing powdered zirconia in an electric furnace with an excess of carbon prepared a substance containing 4 to 5 percent carbon. When this product was heated with more zirconia the carbon disappeared. When rich in carbon, it was rapidly decomposed by air. Later, he mixed powdered zirconia with carbon from sugar using oil and pressed the mass into a cylinder which was then calcined.

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[14] Troost, Preparation of Zr in the Electric Furnace, Compt. Rend., Vol. 116, p. 1227 (1893)

[15] Moissan, H., Reduction by Carbon and Volatilization, Compt. Rend., Vol. 116, p. 1222 (1893)

It was afterwards subjected to a current of 1000 amperes and 50 volts. Varying amounts of carbon were used with the same results. The product had a metallic appearance and was unchanged in moist air even when heated to 100°C. The analysis yielded 88.6% Zr and 11.4% C, agreeing with the formula ZrC. The fact that this composition was maintained when the amount of carbon used was varied indicated that there is some question regarding the ZrC_2 reported by Troost. The Carbide formed had a hardness of 7 to 9.

Becker[16] states that ZrC is easily attacked by N_2 at 1400°C. and up, forming ZrN through decarbonization. He gives the unit cell dimension as 4.76 A° and the density as 6.90. The hardness is given as 8 to 9. The melting point is given as around 3530°C. ZrC has a cubic crystal structure. The specific resistance of ZrC in values of Rho $.10^{-4}$ ohm-cm. at room temperature is given as .634, while at the temperature of liquid air it is given as..378. Thus, at these low temperatures ZrC exhibits a positive temperature coefficient of resistance. The values given for specific resistance at the higher temperatures indicates a positive temperature coefficient of resistance for ZrC at these temperatures also.

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[16] Becker, K., op. cit., pp. 49-68

RAW MATERIALS

The materials used in this work were the four carbides B_4C, TiC, ZrC, and SiC. In forming the test pieces used in the first part of the investigation, Mexico semi-flint clay and grog were used.

The seive analysis of each of these materials is given below:

MESH	B_4C	TiC	ZrC	SiC	Clay	Grog
On 50	11.85 %	0%	11.60 %	0 %	.10 %	22.45 %
" 100	17.45	6.95	24.05	27.40	16.90	44.50
" 170	12.00	.70	13.05	70.40	27.80	15.35
" 200	11.70	18.60	5.15	1.80	14.40	4.55
" 270	19.75	30.70	4.25	.25	24.85	3.55
" 325	1.45	8.80	3.85	.20	6.45	2.10
-325	26.10	34.15	38.05	.05	9.60	7.50
TOTAL	100.30	99.90	100.00	100.10	100.10	100.00

Each of the carbides were examined by means of the x-ray, and all were found to check with the accepted patterns as given in the Hanawalt Tables[17]. On each of the patterns a strong foreign line or peak appeared at a d_hk_l value of 3.38. Since carbon in the form of graphite is usually present along with the carbide, the x-ray pattern for graphite was checked. It was found that graphite has its strongest line at this point, showing that it was present in each of the carbides. Since it was planned to fire the test pieces in a reducing atmosphere, using graphite on the pieces to promote this type of atmosphere, the presence of graphite in the carbides was not thought too objectionable.

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[17] Hanawalt, J. D., Rinn, H. W., and Frevel, L. K., Ind. and Eng. Chem., Anal. Ed., Vol. 10, No. 9, September 15 (1938)

OUTLINE OF WORK

The first study to be attempted in this work was to try to evaluate the effect of the various carbides as additions to a refractory body. The standard refractory body selected was composed of 50% semi-flint clay and 50% grog. Carbide additions were made in 10% increments, first replacing the grog and then the clay, until a total of 70% carbide was added to the body. Since the addition of SiC is known to be beneficial, a series of bodies using SiC was also made to be used as a standard. Thus, four series of bodies were compounded - B_4C, TiC, ZrC, and SiC.

The bodies were made by first thoroughly mixing the ingredients dry and then adding enough water to form a stiff plastic mix. The following test pieces were then formed from each composition: 1"x½"x6" bars, ¼"x½"x4" bars, and 1"x1"x1" cubes. These test pieces were formed by using brass molds. After firing the following tests were to be made on the test pieces: fired shrinkage, deflection under hot load, cold modulus of rupture, bulk density, porosity, temperature coefficient of expansion, resistance to spalling, and temperature coefficient of resistance.

The firing was carried out in an oil fired kiln with care being taken to obtain as nearly as possible a reducing atmosphere. In addition to this, the test pieces were covered with graphite. The firing was carried to 1450°C. (maturing temperature of the refractory body) in ten hours.

RESULTS

None of the bodies fired to a good density other than the standard refractory body and the SiC bodies, so none of the proposed tests could be carried out. The results obtained from this firing may be summarized as follows, based on a visual examination.

Standard Refractory Body - This body fired to a good hardness and density as expected. There were no defects apparent such as bloating. Some of the pieces were stuck to other bars.

Silicon Carbide Body - The same comments as made regarding the refractory body apply also to this body.

Titanium Carbide Body - These bodies fired to a reddish brown color, varying from a light to a darker red as the carbide content increased. Those bodies with the least TiC content appeared to hold their shape well but were very weak, while the higher carbide content bodies were disintegrated.

Zirconium Carbide Body - These bodies disintegrated in all cases. The color varied from a cream color to a dark color depending on the amount of carbide originally in the body.

Boron Carbide Body - These bodies held their approximate shape but seemed to flux badly at the surface with glass being formed there. The glass was light in color. When the test pieces were broken open, the inside seemed to be fired well, with no apparent oxidation of the B_4C evident visually. This may be due to a glass being formed on the surface first, thus preventing further oxidation of the carbide toward the center of the pieces.

The results of the firing based on a microscopic examination may be summarized as follows:

Titanium Carbide Body - The crystalline properties of the material seemed to be absent, as no birefringence could be noted. Under the binocular microscope, the carbide seemed to have disappeared entirely. The material appeared to be covered with a glassy material.

Zirconium Carbide Body - Here again the crystalline properties of the material seemed to be absent. No conclusive evidence regarding the effects of the firing could be determined. A glassy appearance seemed apparent in this body also.

Boron Carbide Body - The material toward the center or away from the surface of the test pieces seemed to have retained its crystalline nature. In appearance it looked the same as the unfired material. Under the binocular microscope, the material in a freshly fractured surface showed a minimum of glass, although sections appeared to have turned to glass entirely (appeared very much like glass inclusions). What appeared to be B_4C particles were dispersed throughout the surface. The surface appeared to be vesicular with very minute holes over the surface. These may be due to oxidation of B_4C with the excaping gas causing the holes. When a section was viewed with the glassy surface in cross-section, the glassy surface appeared as a definite glass layer over the surface. This clearly showed the formation of a glass surface on the outer surfaces of the test pieces. In places the glass penetrated from the surface into the body.

Samples from the fired bodies were examined by x-ray diffraction means, and the results are presented in graphic form in Figures 1, 2, and 3. The interplanar spacing value d_{hkl} is plotted along the horizontal axis, and the relative intensity is plotted along the vertical axis. The strongest line in each pattern is given an intensity value of one (1), and the other lines are given an intensity relative to the strong line. The x-ray patterns were made using a Geiger-Muller Tube X-ray Spectrometer using Cu K-alpha radiation and a Ni filter. All patterns were made using the same conditions on the x-ray apparatus. The results based on an examination by x-ray methods may be summarized as follows:

Zirconium Carbide Body - In Figure 1, A is the pattern of unfired ZrC, B is one sample of the fired body which was of a light color, and C is another sample which was of a darker color. By an examination of Figure 1, it can easily be seen that the ZrC has been completely destroyed, since the characteristic lines of ZrC have disappeared from the other patterns. Some of the lines seem to be present but the differences in relative intensities precludes this possibility. Since clay and grog are also present in the bodies, it would be difficult to determine what compounds are present after firing, due to the presence of too many different compounds.

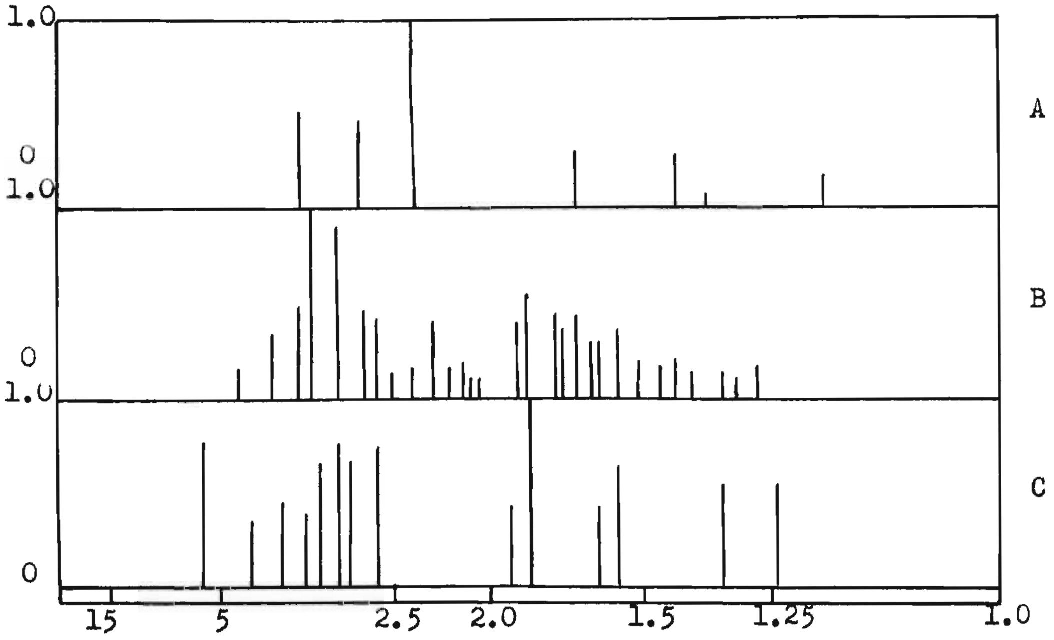
Titanium Carbide Body - In Figure 2, A is the pattern of the unfired TiC, B is one sample of the fired body which was reddish in color and fairly hard, and C is another sample which had disintegrated in firing. By examination of Figure 2 it can be seen that the characteristic TiC lines are absent from B and C. Here also some of the lines of TiC seem to have been retained in B and C, but the relative intensities are not correct.

Boron Carbide Body - In Figure 3, A is the pattern of unfired B_4C, and B is a sample of a B_4C body taken from the center of the test piece. The absence of characteristic B_4C lines in B indicates the change of the B_4C to another form.

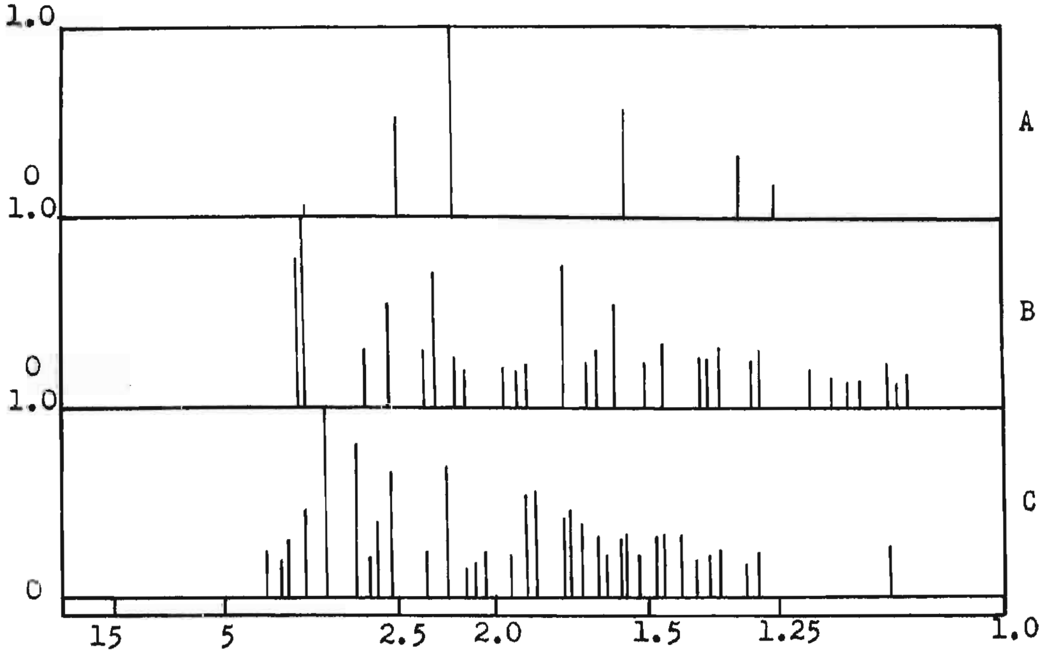
CONCLUSIONS

The results indicate that the atmosphere present in the kiln was definitely oxidizing, at least at the higher temperatures. The ZrC and TiC bodies by their visual appearance and x-ray diffraction results seem to oxidize most rapidly of all of the carbides tested. The fact that these bodies disintegrated badly may be accounted for if it is assumed that they formed an oxide upon oxidizing. Since the unit cell dimensions of the oxides are greater than that of the carbides, and expansion and resultant disintegration would take place. The glassy material formed on the Boron Carbide bodies seems to indicate an oxidation of the B_4C to B_2O_3 with a resultant glass formation. By visual inspection these bodies appeared to have unchanged B_4C material in the center of the test pieces, indicating that the glass layer on the surface retarded exidation of the B_4C underneath. Since the x-ray evidence failed to reveal any B_4C present, however, it appears that the B_4C has at least changed form if it has not been oxidized. From this test, it may be concluded that these carbides are susceptible to attack by oxygen at higher temperatures, the degree of susceptibility being indeterminate from this test. Also, ZrC and TiC are more readily attacked by oxygen than is B_4C.

To test the carbides with regard to their behavior when fired in



d in A°
FIGURE ONE



d in A°
FIGURE TWO

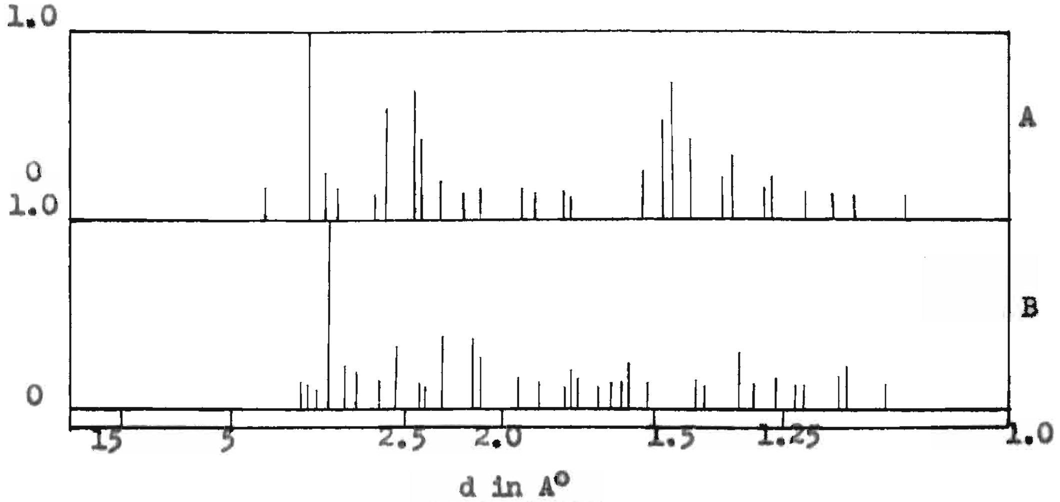


FIGURE THREE

a reducing atmosphere, samples of the carbides as received were fired to 1200°C. in a Hayes gas-flame curtain type of furnace. After firing, samples of each of the carbides were examined by x-ray diffraction methods, using the same apparatus as described above. The results of this test are shown in graphic form in Figures 4, 5, and 6.

RESULTS

Titanium Carbide - In Figure 4, A is a pattern of a sample of unfired TiC, B is a pattern of a sample of TiC fired to 1200°C. for one hour under reducing conditions, and C is a pattern of a sample of TiC fired to 1200°C. for ten hours under oxidizing conditions (taken from a subsequent test). From an examination of Figure 4 it is seen that the characteristic lines of TiC remain in B, and that other lines have also made their appearance. This would indicate that some of the carbide has changed to another compound while some of it retains its original form. A lot of the lines in B agree with C, which is actually a pattern of TiO_2, indicating that the change has been one due to oxidation. Visually, the TiC expanded to approximately double its original volume and changed to a light color which also indicates an oxidation reaction.

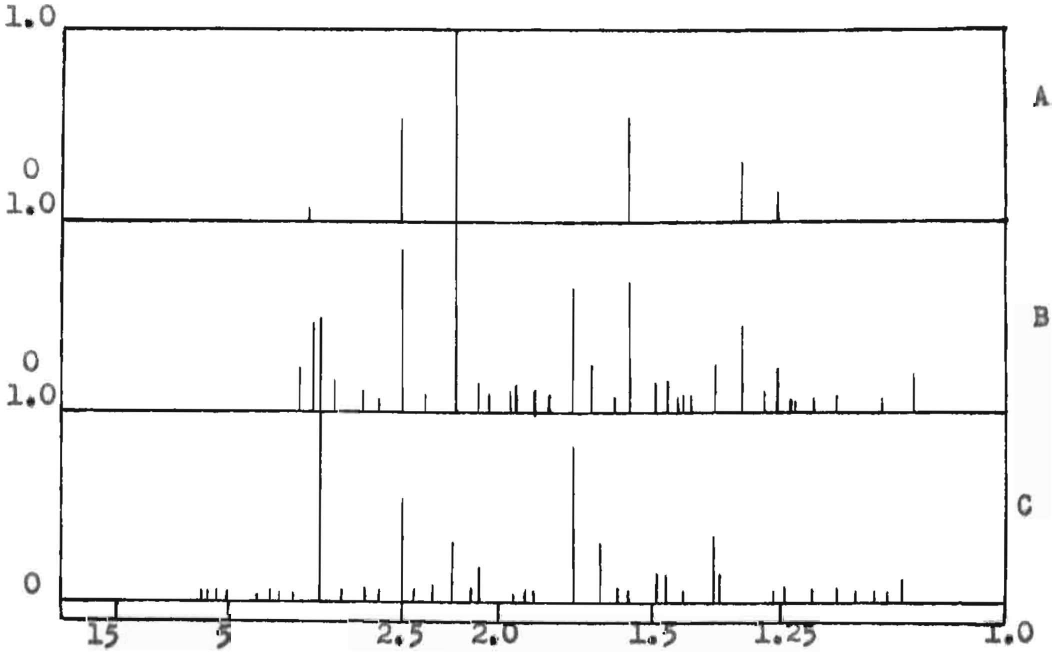
Zirconium Carbide - In Figure 5, A is a pattern of a sample of unfired ZrC, B is a pattern of a sample of ZrC fired to 1200°C. for one hour in a reducing atmosphere, and C is a pattern of a sample of ZrC fired to 1200°C. for ten hours in an oxidizing atmosphere. (taken from a subsequent test). From an examination of Figure 5 it is seen that some of the lines of pure ZrC check those of B. Here also though, the presence of other lines indicates the presence of other materials. Some of the foreign lines check the pattern C. This indicates an oxidation of the carbide. The ZrC appeared to have expanded approximately double its original volume and changed to a light color, again indicating an oxidation reaction.

Boron Carbide - In Figure 6, A is a pattern of a sample of unfired B_4C, and B is a pattern of a sample of B_4C fired to 1200°C. for one hour in a reducing atmosphere. An examination of Figure 6 shows that few of the lines check the pattern of the pure carbide. The carbide did not change color or volume enough to be observed visually, but it did form a hard mass at the bottom of the crucible, indicating a possible slight oxidation of the B_4C.

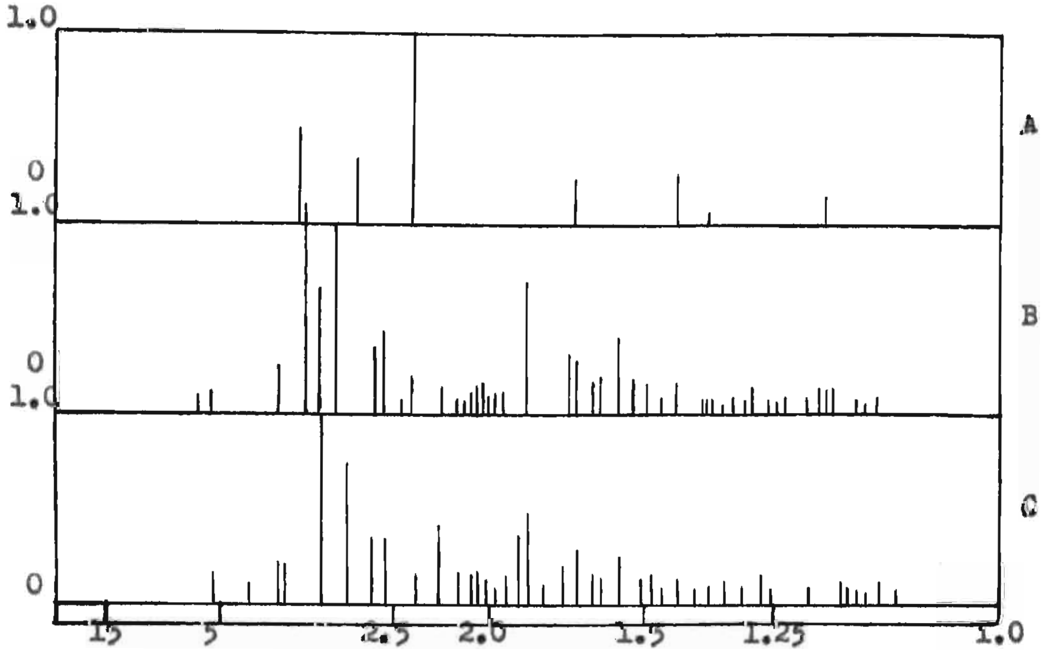
CONCLUSIONS

It appears that a small amount of oxygen must have been present in the firing atmosphere in spite of the gas-flame curtain used. This would indicate that the carbides, especially ZrC and TiC, are very susceptible to oxygen in small amounts. The gas used in this furnace to give the curtain is a coal gas which tends to break down into several gaseous components at higher temperatures. This presents ths possibility that the carbides may have been affected by gasses other than oxygen, but this is unlikely since the products of the firing seem to be oxides.

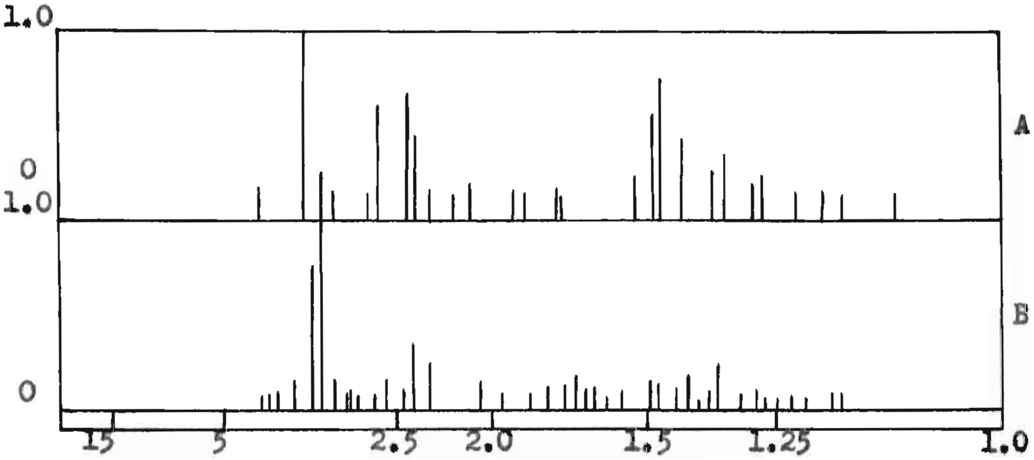
Since the carbides seem to be very sensitive to oxygen, it was thought that some useful information might be obtained by determining their reaction with oxygen at various temperatures. Since B_4C seems to have been investigated thoroughly already, this last part of the work was restricted to ZrC and TiC.



D in A°
FIGURE FOUR



d in A°
FIGURE FIVE



d in A°

FIGURE SIX

Fractions of ZrC and TiC below 325 mesh in size were obtained for a study of their behavior under oxidizing conditions at various temperatures. Samples of ZrC were fired in air at temperatures of 400°, 450°, 500°, 600°, 700°, 800°, 900°, 1000°, 1100°, and 1200°C for ten hours. This prolonged period of heating was selected to allow any changes that might take place to more or less go to completion. Samples of TiC were fired in air at temperatures of 300°, 350°, 400°, 500°, 600°, 700°, 800°, 900°, 1000°, 1100°, and 1200°C. for ten hours. The prolonged heating period was selected for the same reason given above.

After heat treatment x-ray patterns of the various samples were made using the same apparatus described previously. The patterns obtained were then compared with the pure ZrC, pure TiC, and the various oxide patterns of ZrO_2 and TiO_2. The graphical representations of these patterns are given in Figures 7(a-b) and 8(a-b). Figure 7 gives those patterns obtained from the ZrC samples, and Figure 8 shows those obtained from the TiC samples.

In Figure 7(a), A represents the pure ZrC pattern, B is the pattern of ZrC heated to 400°C., C is the 450°C. pattern, D is the 500°C. pattern, E is the 600°C. pattern, F is the pattern of tetragonal ZrO_2, G is the pattern of monoclinic ZrO_2 (will be called #1 when referred to henceforth), and H is the pattern of monoclinic ZrO_2 (will be called #2 when referred to henceforth).

In Figure 7(b), A represents the pattern of ZrC heated to 700°C., B is the 800°C. pattern, C is the 900°C. pattern, D is the 1000°C. pattern, E is the 1100°C. pattern, F is the 1200°C. pattern, G is the pattern of monoclinic ZrO_2 #1, and H is the pattern of monoclinic ZrO_2 #2.

In Figure 8(a), A represents the pure TiC pattern, B is the pattern of the 300°C. sample of TiC, C is the 350°C. pattern, D is the 400°C. pattern, E is the 500°C. pattern, F is the pattern of Anatase, B is the pattern of Rutile, and H is the pattern of Brookite.

In Figure 8(b), A is the pattern of TiC fired to 600°C., B is the 700°C. pattern, C is the 800°C. pattern, D is the 900°C. pattern, E is the 1000°C. pattern, F is the 1100°C. pattern, G is the 1200°C. pattern, H is the pattern of anatase, and I is the pattern of Rutile.

The patterns of the oxides were taken from the card file published jointly by the American Society for Testing Materials and the Committee on X-ray and Electron Diffraction of the Division of Chemistry and Chemical Technology of the National Research Council.

Since the oxides of ZrO_2 are formed on heating, a short review of literature on the forms of ZrO_2 was made. G. L. Clark and D. H. Reynolds[18] found that when $ZrOCl_2 \cdot H_2O$ was heated between 300°C and 500°C., it formed ZrO_2. The tetragonal form of ZrO_2 forms at 500°C. and is converted monoclinic Baddelyite above 600°C. When Zirconyl Hydroxide is heated at 650°C., it first forms tetragonal ZrO_2 which then is converted to the monoclinic form irreversibly, complete conversion requiring a long period of time. When heated at 500°C., the Zirconyl Hydroxide forms tetragonal ZrO_2 which shows no tendency to change to monoclinic even with long heating.

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[18] Clark, G. L. and Reynolds, D. H., Ind Eng. Chem., Vol. 29, (6), pp. 711-15, (1937)

O. Ruff and F. Ebert[19] state that the oxide formed from heating the nitrate, oxalate, or basic chloride of Zr below about 600°C. is tetragonal but metastable, becoming monoclinic above 600°C.

Bunting[20] states that anatase is formed whenever Titanium Hydroxides are heated to a temperature below about 900°C. Anatase is formed by heating the hydroxide around 400°C. On heating above 1000°C., pure rutile is formed. He states that if there is a temperature where rutile is in stable equilibrium with anatase and brookite, it is below 400°C. The white color of anatase changes to a light tan when it changes to rutile, and the color darkens as the rutile is heated to higher temperatures, becoming blue-black on melting.

The constants (taken from the card file mentioned previously) for tetragonal ZrO_2 are: a_o- 5.07 and c_o- 5.16. The constants for monoclinic ZrO_2 #1 are: a_o- 5.21, b_o- 5.26, c_o- 5.37, and B - 80°32'. The constants for monoclinic ZrO_2 #2 are: a_o- 5.17, b_o- 5.26, c_o- 5.30, and B - 80.8°.

RESULTS

As can be seen from the graphical representation in Figure 7(a-b) of the x-ray patterns of samples of pure ZrC fired for 10 hours in air at various temperatures, a breakdown of ZrC is not apparent until a temperature of 450°C. is reached. From the temperatures used, this

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[19] Ruff, O. and Ebert, F., Ceramics of Highly Refractory Materials, Z. Anorg. Chem., Volume 180, pp. 19-41 (1929)

[20] Bunting, E. N., Phase Equilibria in the Systems TiO_2, TiO_2-SiO_2, and TiO_2-Al_2O_3, U. S. Bur. of Stds., Jour of Res., Res. Paper R P 619, Vol. 11, November (1933).

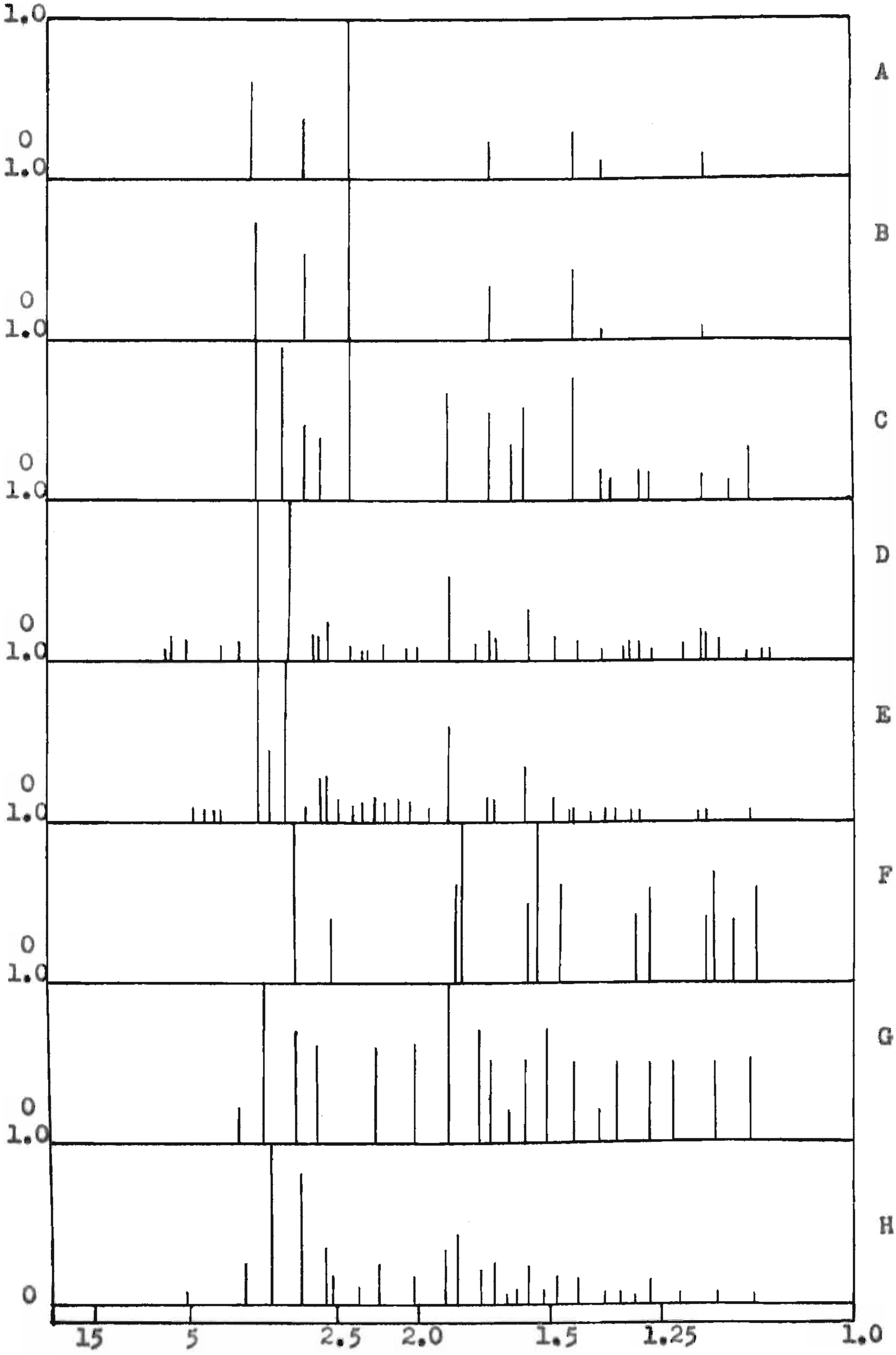
indicates that ZrC begins to oxidize somewhere between 400°C. and 450°C. The change in ZrC is to the tetragonal form of ZrO_2 at 450°C. This change is not complete at this temperature, as evidenced by the presence of ZrC lines in the x-ray pattern.

The x-ray pattern of ZrC fired to 500°C. for 10 hours shows other weak lines beginning to make their appearance, indicating the beginning of the formation of another compound here. There seems to be some correlation between these new lines and the lines of the pattern of monoclinic ZrO_2 #1. In this pattern also, it seems that the ZrC is not completely oxidized as some weak lines appear to check the pattern for ZrC. Thus, this pattern appears to be largely tetragonal ZrO_2, with possibly some monoclinic ZrO_2 #1 and ZrC present also.

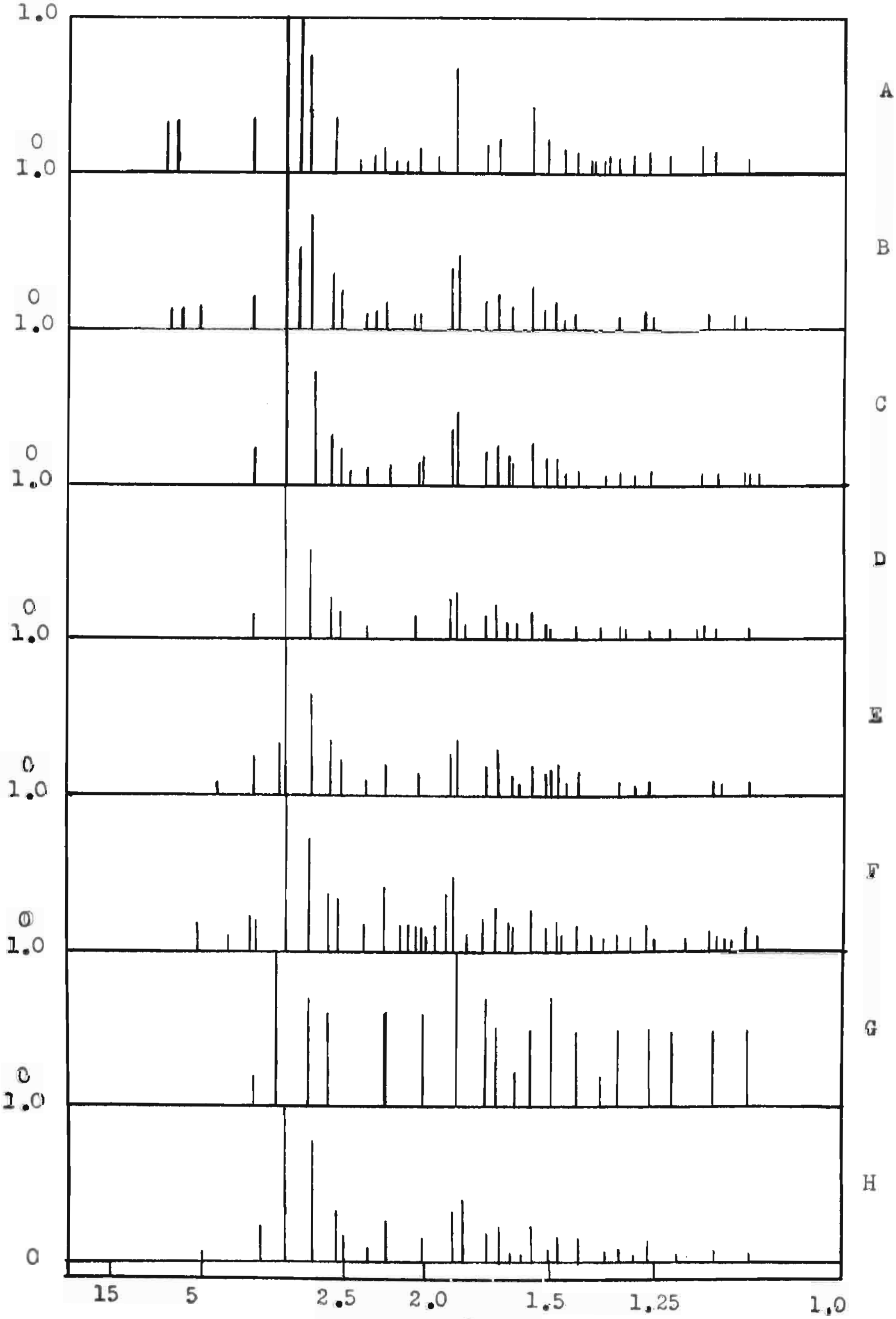
In the 600°C. pattern, the sample appears to have been oxidized completely to monoclinic ZrO_2. It also appears that both monoclinic ZrO_2 patterns are present here, with the pattern of monoclinic #1 predominating.

The 700°C. pattern is essentially the same as the 600°C. pattern, except that the amount of monoclinic ZrO_2 #2 appears to be increasing. The 800°C. pattern shows this increase becoming more pronounced. The 900°, 1000°, 1100°, and 1200°C. patterns show that the ZrC has converted completely to the monoclinic ZrO_2 #2 form.

From the graphical representations in Figure 8(a-b) of the x-ray patterns of samples of pure TiC fired for 10 hours in air at various temperatures, it can be seen that a breakdown of TiC is not apparent until a temperature of 350°C. is reached. From the temperatures



d in A°
FIGURE SEVEN (a)



d IN A°
FIGURE SEVEN (b)

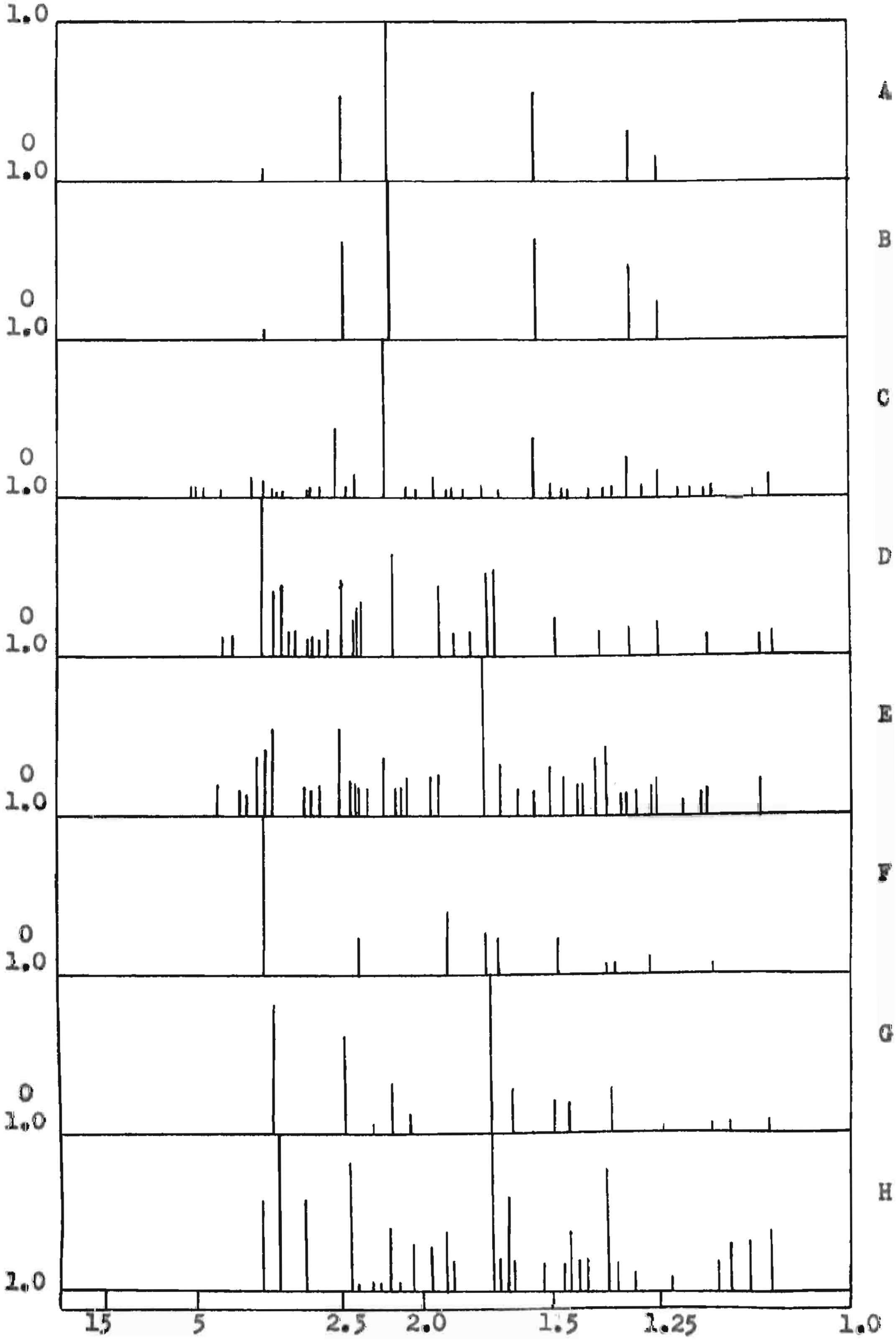


FIGURE EIGHT (a)

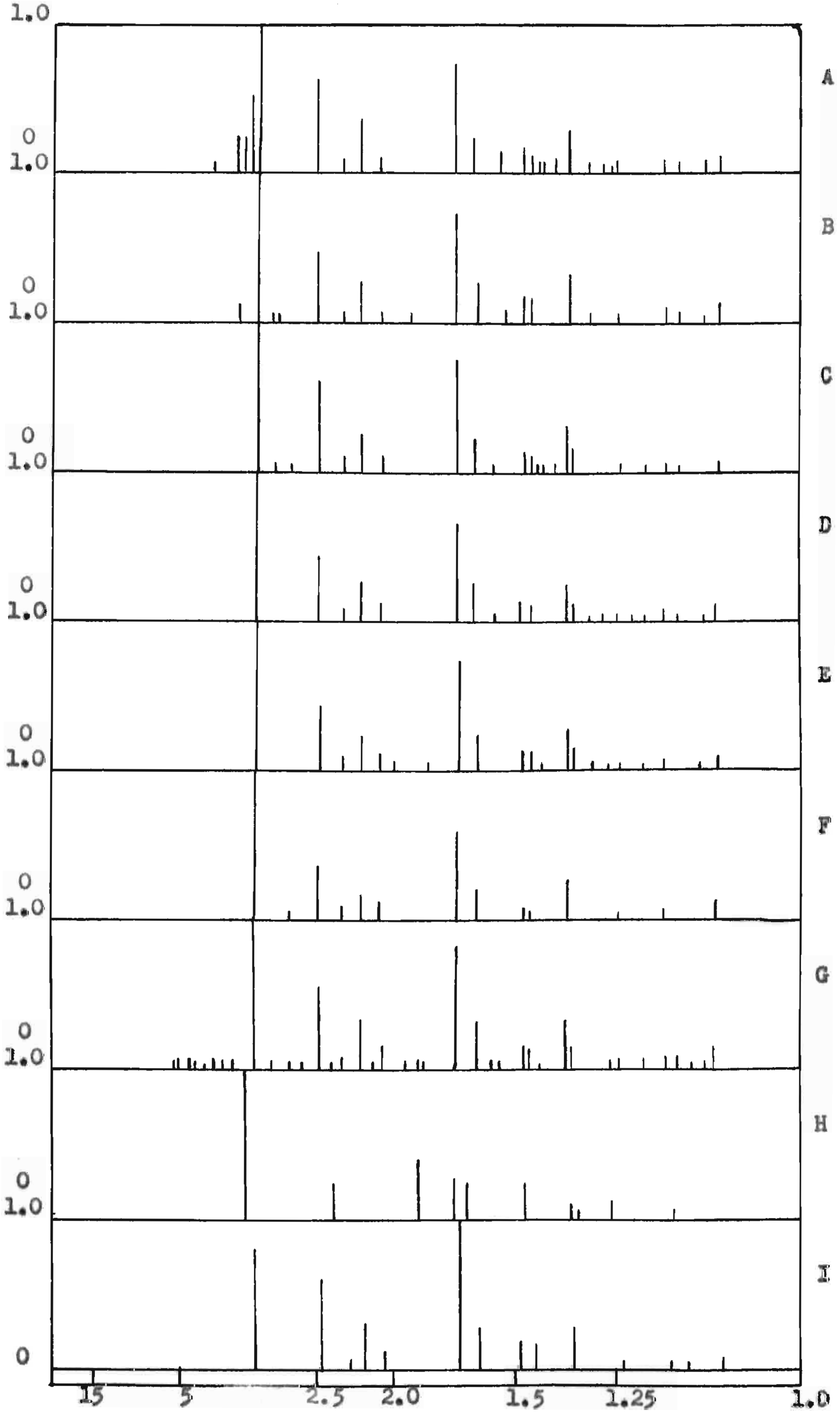


FIGURE EIGHT (b)

used, this indicates that TiC begins to oxidize somewhere between 300°C. and 350°C. The change in TiC at 350°C appears to be to Anatase, a form of TiO_2. The change is not complete at this temperature as evicenced by the presence of lines of TiC.

The x-ray pattern of TiC fired to 400°C. for 10 hours shows other lines making their appearance. By comparing this pattern with those of the oxides, it appears that at this temperature all of the oxides are present. This seems to be especially well shown by the three lines appearing between d values of 3 and 4.

The x-ray pattern of TiC fired to 500°C. for 10 hours seems to show a reduction in the amount of Anatase present and an increase in the amount of Rutile present. Brookite seems to be present here also as evidenced by the lines appearing between d values of 3 and 4.

The x-ray pattern of TiC fired to 600°C. for 10 hours shows the presence of Rutile alone. This is true also for the remainder of the patterns.

CONCLUSIONS

The ZrC appears to begin to oxidize at a temperature of 450°C. The material changed to tetragonal ZrO_2 at this temperature, and at 500°C. seemed to begin changing over to monoclinic ZrO_2 #1. At 600°C. the material was entirely monoclinic ZrO_2 of two forms, with the monoclinic #1 predominating over the monoclinic #2. As the temperature was increased the amount of monoclinic ZrO_2 #2 increased, until at the temperature of 900°C., the material was entirely monoclinic ZrO_2 #2. The results obtained indicate that ZrC is rapidly affected by air after a temperature between 400°C. and 450°C. is reached. The changes taking place upon oxidation seemed to check the changes in ZrO_2 reported in the literature, with the exception that the tetragonal form of ZrO_2 seems to begin forming at a slightly lower temperature than previously reported. Also, no mention was made in the literature reviewed regarding the change occurring in the monoclinic forms of ZrO_2

The TiC appears to begin to oxidize at a temperature of 350°C. The material changed to Anatase at this temperature, and at 400°C. all of the oxides of TiO_2 appear to be present. At 500°C., all of the oxides again seem to be present, but with Rutile predominating. From 600°C. up, Rutile alone seems to be present. The results indicate that TiC is rapidly affected by air after a temperature between 300°C. and 350°C. is reached. The changes taking place upon oxidation seem to check the literature well with the exception that the three oxides appear to be present together to a slight degree at 500°C. Also, the TiC changes to Rutile at 600°C. completely while it was reported that Rutile forms at 900°C.

To complete a picture of the firing behavior of the ZrC and TiC in air, it was thought that an investigation of the oxidation rates of the two materials might prove interesting and valuable. The method selected for determining these rates was to make use of the x-ray apparatus for quantitative determinations of the ZrC and TiC content of fired samples.

In making quantitative analyses by x-ray diffraction methods, it is necessary to prepare a curve of intensity ratio plotted against percentage composition. In doing this, it is necessary to choose a reference material which will produce a strong diffraction line within two degrees (Bragg angle of 2Θ) or so of a strong line produced by the material to be determined. In addition to this, another crystalline material must be selected as a filler substance, so that various percent compositions of the material to be determined may be compounded. This last material must be selected on the basis that it will not produce a diffraction line near the lines produced by the standard reference material or the material to be determined. When the reference material and filler material are selected, a series of compositions, ranging from 0% to 100% of material to be determined, are compounded with the filler substance and with a standard amount of reference material added. These compositions are then thoroughly and intimately mixed and made into an x-ray sample, after which a pattern or a specific segment of a pattern is made. From the pattern, the intensities of the reference line and the line of the material to be determined are found. By plotting the ratio of intensities of material to be determined over reference material against the percentage of material to be determined, a curve is obtained. In dealing with an unknown sample, all that is necessary is to add the standard amount of reference material to the sample, mix intimately, and obtain the desired segment of the pattern. From the pattern, the above intensity ratio may be determined. By using this ratio and the previously obtained curve, the percentage of the material to be determined may be found.

In determining the standard curve for ZrC, KCl was selected as the reference material or internal standard, and it was decided to add it in the ratio of 0.2 grams of KCl per gram of sample. KCl produces a diffraction line at the angle 2θ of 40° 40', and the intensity of this line is to be compared with that of the line produced by ZrC occuring at the angle 20 of 38° 20'. The filler material selected was CaF_2, since this material does not produce a diffraction line near the lines of KCl and ZrC which are to be compared.

In obtaining the standard curve for ZrC it was necessary to correct the percent ZrC in each sample to account for the amount of free carbon present in the original ZrC. By firing a known weight of ZrC to 1200°C for 10 hours so as to change it completely to ZrO_2, and determining the weight of ZrO_2, it was possible to determine the amount of free carbon present in the ZrC. This was found to be approximately 10% free carbon. After correcting for this, the curve shown in Figure 9 was obtained. The data corresponding to this curve and obtained from the x-ray patterns of the standard samples is as follows:

% ZrC	Intensity ZrC	Intensity KCl	I(ZrC)/I(KCl)
90	160	27	5.93
81	139	26	5.35
72	140	28	5.00
63	146	38	3.84
54	110	30	3.67
45	76	22	3.45
36	63	22	2.86
27	64	26	2.46
18	37	29	1.28
9	33	37	.89

The internal standard selected for obtaining the TiC standard curve was NaF, since it produced a diffraction line at the angle 20 of 38° 40' to be compared in intensity with one produced by TiC at the angle 20 of 41° 40'. The NaF was added in the ratio of 0.2 grams NaF per gram of sample. The filler substance selected was CaF_2 for the same reason as given above. The amount of free carbon in the TiC was quite small as evidenced by the low intensity of the carbon line in the x-ray patterns of TiC. Therefore, no correction was made for the amount present. The standard curve for TiC is shown in Figure 11, and the data corresponding to this curve is as follows:

%TiC	Intensity TiC	Intensity NaF	I(TiC)/I(NaF)
100	123	36	3.42
90	108	34	3.18
80	93	32	2.90
70	103	37	2.78
60	73	30	2.43
50	58	32	1.81
40	59	43	1.37
30	42	40	1.05
20	40	43	.93
10	14	40	.35

After obtaining the standard curves, samples of -325 mesh ZrC were fired at 450, 500, 600, and 700°C. for times of 5 minutes, 15 minutes, 30 minutes, 1 hour, and 2 hours at each temperature. Approximately 2 grams ZrC was used for each sample, and the firing was done in a flat crucible. After adding the standard amount of internal standard to each sample and mixing thoroughly, x-ray patterns of the segment containing the desired lines were made of each sample. The same setting on the x-ray apparatus was used in obtaining these patterns as was used in obtaining the standard curve. The intensity ratio described above was obtained for each pattern, and from this the percent ZrC present after each firing was determined. Curves were then plotted for each temperature of percent ZrC present versus time of firing. These curves are shown in Figure 10.

Samples of TiC were fired at temperatures of 350, 400, and

600°C. for periods of time of 5 minutes, 15 minutes, 30 minutes, 1 hour, and 2 hours. The same procedure was followed for determining percentage as described for ZrC, with the exception that NaF is used as the internal standard. The curves obtained are shown in Figure 12.

The data for these curves is as follows:

Time	Intensity ZrC	Intensity KCl	I(ZrC)/I(KCl)	% ZrC
		ZrC-450°C.		
5 Min.	39	19	2.05	31
15	36	21	1.71	26
30	31	22	1.41	21
2 Hr.	11	19	.58	8.5
		ZrC-500°C.		
5 Min.	49	26	1.88	28
15	35	20	1.75	25
30	16	16	1.00	15
1 Hr.	12	18	.67	9.5
2	14	27	.52	7.5
		ZrC-600°C.		
5 Min.	18	20	.90	8.5
15	7	17	.41	5.5
30	0	17	.00	0.0
		ZrC-700°C.		
5 Min.	4	25	.16	2
15	0	19	.00	0.0

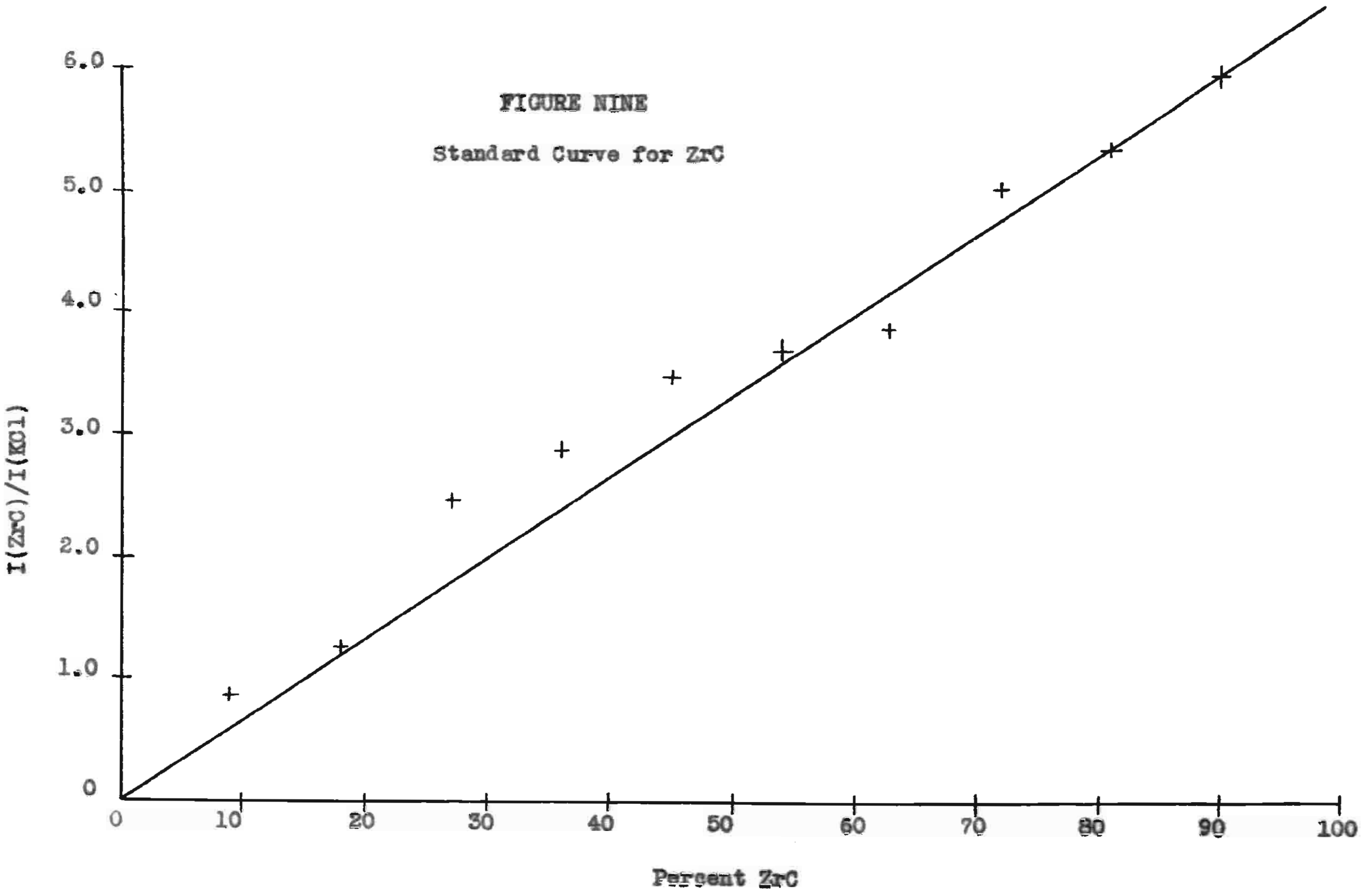


FIGURE NINE

Standard Curve for ZrC

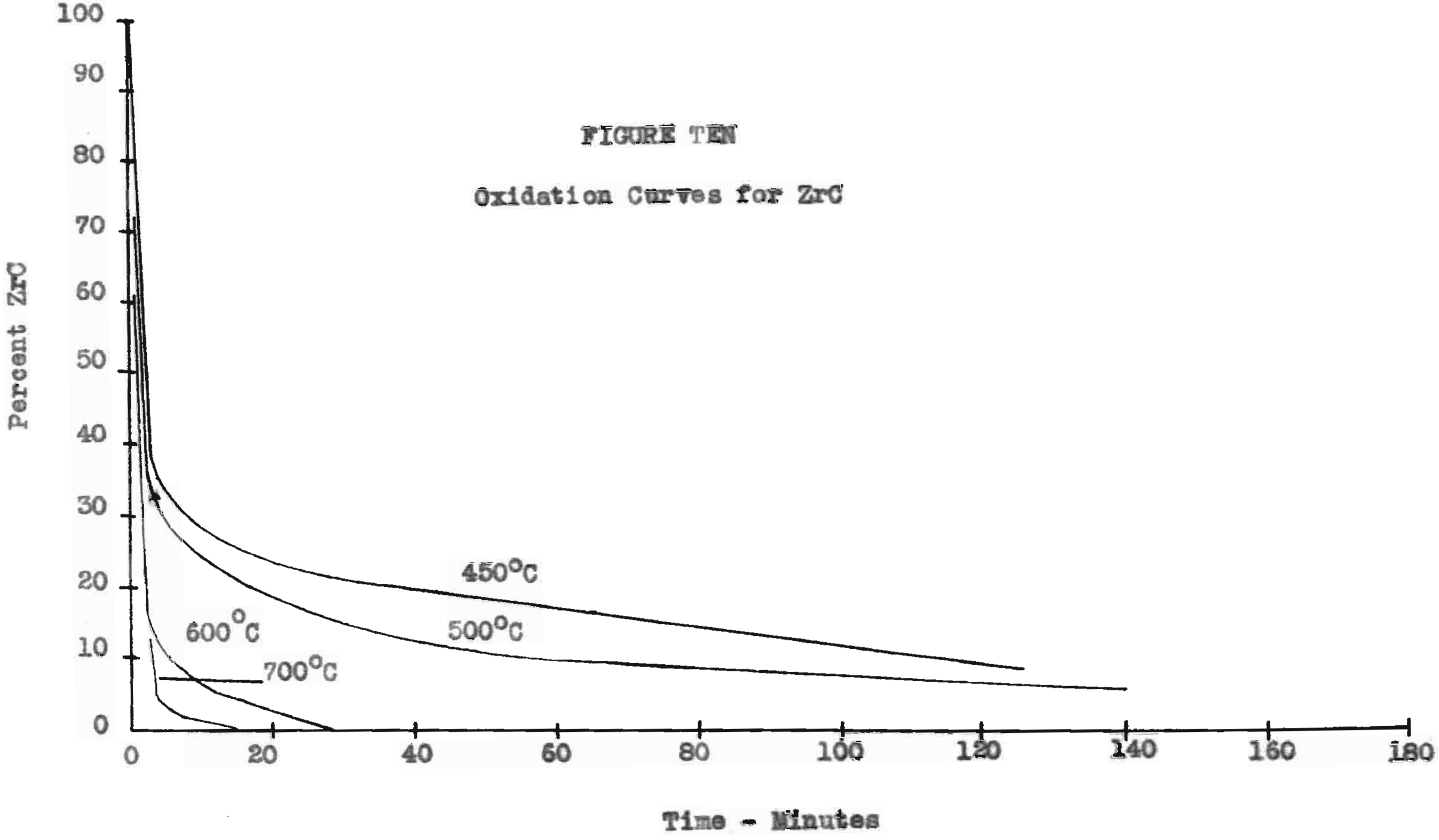


FIGURE TEN

Oxidation Curves for ZrC

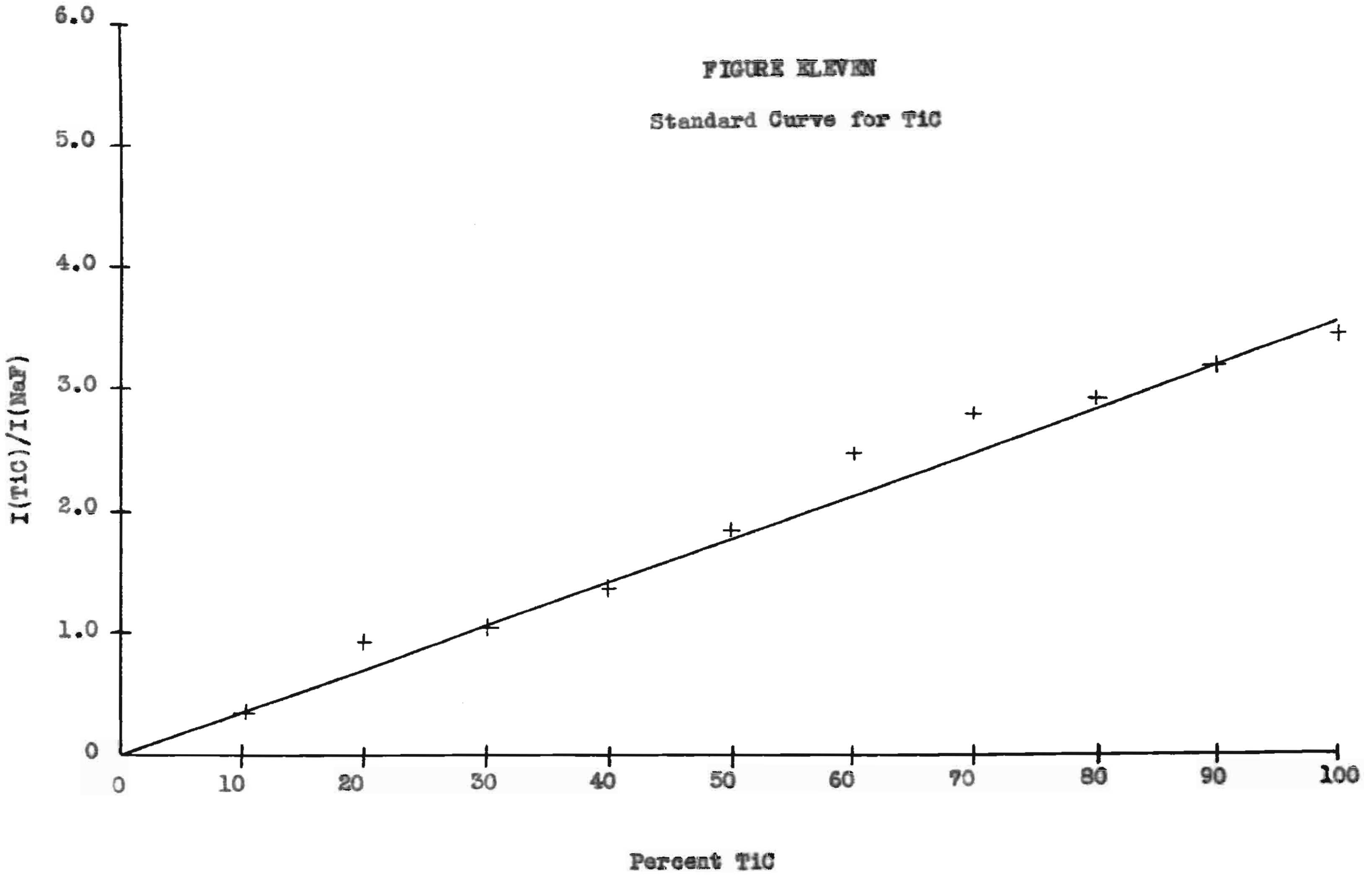


FIGURE ELEVEN

Standard Curve for TiC

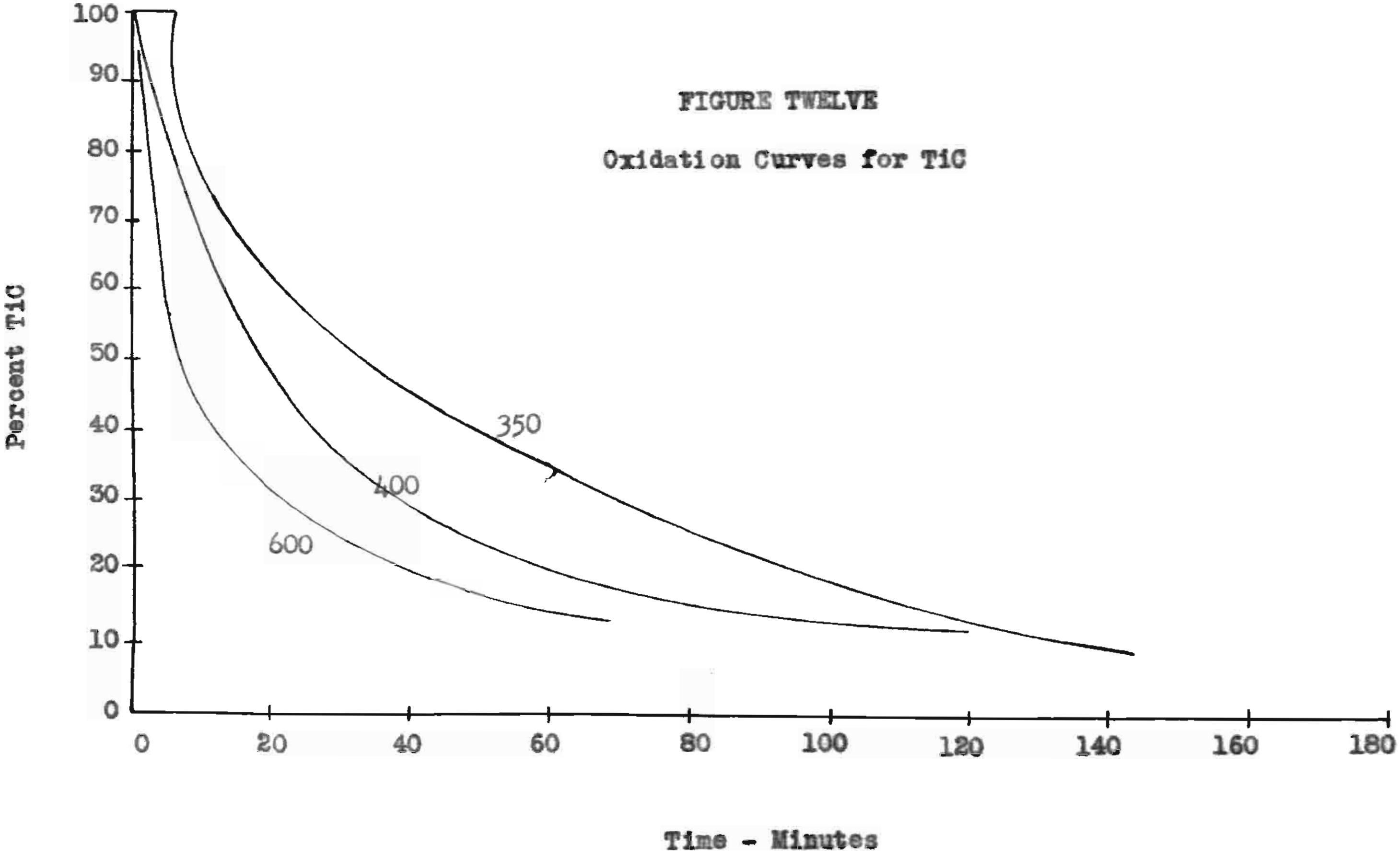


FIGURE TWELVE

Oxidation Curves for TiC

TiC-350°C.

Time	Intensity TiC	Intensity NaF	I(TiC)/I(NaF)	% TiC
5 Min.	96	26	3.69	100
15	70	30	2.33	66
30	74	35	2.11	59.5
1 Hr.	51	42	1.21	34
2	16	38	.42	12
		TiC-400°C.		
5 Min.	78	28	2.79	79
15	82	42	1.95	54
30	45	35	1.29	36
1 Hr.	26	42	.62	17
2	17	42	.41	11.5
		TiC-600°C.		
5 Min.	76	37	2.06	58
15	50	29	1.78	48
30	27	33	.75	23
1 Hr.	19	37	.51	14

RESULTS

The curves and data indicate that as soon as the breakdown temperature is reached, rapid oxidation of both ZrC and TiC occurs. The rate of oxidation in both instances increases as the temperature increases. Also, in both instances the rate of oxidation is rapid at the beginning but later slows down at all temperatures. A comparison of the curves seems to indicate that ZrC oxidizes more rapidly than TiC even though it does not break down until a slightly higher temperature is reached. It was noted in firing that the ZrC seemed to glow brightly even at the lower temperatures and continue to glow after removal from the furnace, indicating a violent exothermic reaction. This may account for the more rapid oxidation rate of ZrC.

CONCLUSIONS

ZrC and TiC oxidize rapidly when their breakdown temperature is reached. The rate of oxidation increases with an increase in temperature. The oxidation rates of ZrC and TiC indicate a great susceptibility to an oxidizing atmosphere.

As a final summary, it may be said that the results of each of the investigations presented in this paper indicate that apparently, for the reasons given in the results, ZrC and TiC cannot be used as high temperature refractory materials.

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