Cermets From Thermite Reactions

J. D. Walton, Jr. and N. E. Poulos

Georgia Institute of Technology
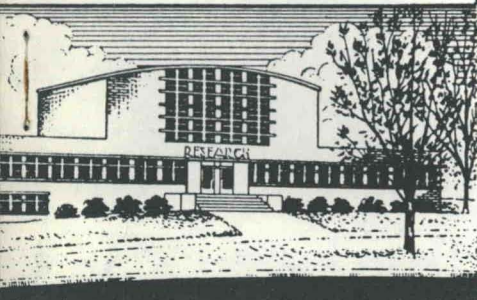
Engineering Experiment Station

Georgia Institute of Technology

Atlanta, Georgia

Cermets From Thermite Reactions

by J. D. WALTON, JR., and N. E. POULOS

Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia

The process whereby the components of a thermite are pressed into a desired shape and ignited to form a cermet is described. In this process, the oxide of the cermet (Al_2O_3) is produced from the oxidation of powdered aluminum and the metallic phase is produced from the resulting reduction of its oxide. A third component (clay, Al_2O_3, or MgO) is added to act as a control agent. Methods of compacting and firing are described. A table of oxides reduced by aluminum using this process is presented. The formation of metallic silicides and borides as the metallic phase of a cermet from the appropriate silicates and borates, or metallic oxides with silica or boric acid, is discussed. As an example, $ZrSi_2$ is produced by the reduction of either $ZrSiO_4$ or ZrO_2 and SiO_2, and TiB_2 by the reduction of TiO_2 and B_2O_3. The following advantages may be obtained by this method: (1) inexpensive compositions, (2) low ignition temperatures (1800°F.), (3) high reaction temperatures (5000°F.), (4) short firing time (1 hour), and (5) controlled atmosphere unnecessary. A technique was developed whereby cermet test specimens could be prepared from the thermite reaction between aluminum and zirconium silicate. The tensile strength of the finished cermet is given at room temperature and at 2200°F. The apparatus used for determining these tensile strengths is described. Modulus of rupture data also are given. Other oxide thermites were added to the basic zirconium silicate thermite mixture. The effect of these thermite additions on the strength of the basic thermite is described.

I. Introduction

ONE of the primary objectives of this investigation was the production of a high-temperature-resistant coating on a lower-melting metallic substrate.

As a first attempt to accomplish this objective, the following approach was taken: (1) A coating with the required high melting point and thermal expansion was selected, (2) this coating was thoroughly mixed in powdered form with the ingredients of a thermite, applied to the metallic substrate in the form of a paste, and oven dried, and (3) the coated metal was placed in a furnace and heated to the ignition temperature of the thermite. It was assumed that the heat developed within the coating as a result of the ignition of the thermite would be sufficient to melt the coating itself. The short duration of the thermite reaction and the high heat
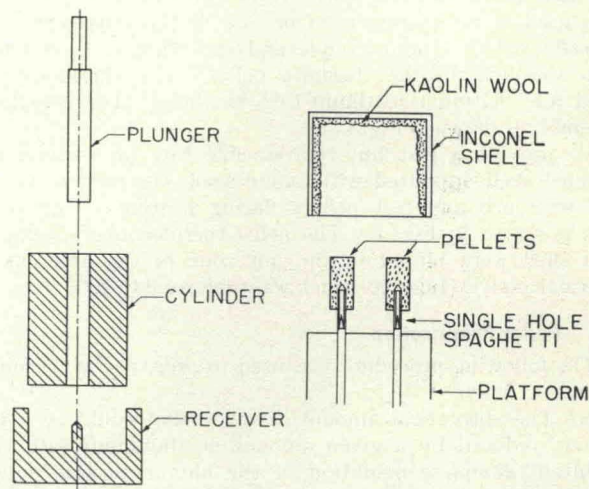

Fig. 1. Compacting die and pellet assembly for differential thermal analysis.

capacity of the metallic substrate would protect the substrate from damage.

The thermite constituent of the preliminary coating not only provided the desired heat to produce fusion of the coating but did in fact result in the formation of a cermet-type material. It was felt that this technique could be extended to provide a new method of producing high-temperature-resistant cermet bodies. It soon became evident, however, that much basic information was lacking concerning the heat which could be developed from a thermite reaction as related to the oxide or oxides used, their particle size, and the particle size of the aluminum used. There was even some question as to what oxides could be used successfully in such a thermite reaction. It therefore was decided that the thermite reactants would be fabricated into a suitable test specimen for study of the pertinent variables that should affect the body resulting from the ignition of the thermite.

II. Experimental Procedure

(1) Apparatus and Method of Test

For a better evaluation of the thermite components to be used in the proposed coatings, it was felt that the following properties of the thermite reaction should be known: (1) the temperature at which the reaction was initiated, (2) the intensity of the reaction, (3) the duration of the reaction, and (4) the nature of the reaction products.

A laboratory apparatus that could be used to provide much of the desired information was the differential thermal analysis equipment.[1] The technique selected was one in

[1] J. D. Walton, Jr., "New Method of Preparing Clay Samples for Differential Thermal Analysis," *J. Am. Ceram. Soc.*, **38** [12] 438–43 (1955).

which the material to be studied was pressed into the shape of a cylindrical pellet approximately $^5/_8$ in. long and $^3/_8$ in. in diameter with a hole in one end to receive the thermocouple and supporting spaghetti. With this technique, the block or specimen holder was eliminated, allowing easy removal of the spent thermite from the thermocouple. To remove the thermocouple from the direct heat of the thermite reaction, a modification of the thermocouple-spaghetti support system was required for the thermite pellet. A piece of one-hole spaghetti of the same outside diameter as the two-hole spaghetti carrying the thermocouple was used as an extension. One end of this extension was placed over the thermocouple and the other end extended into the hole in the thermite pellet. The thermocouple used was platinum–platinum-13% rhodium. The complete assembly is shown in Fig. 1.

To provide a fast but reproducible rate of heating, an Inconel shell, insulated with kaolin wool, was used to cover the reference and test pellets during heating. This shell also is shown in Fig. 1. The pellet-thermocouple assembly and shell were placed in the hot zone of the differential thermal analysis furnace, which was preheated to 2000°F.

(2) Pellet Preparation

The following procedure was used to prepare the thermite pellets:

(1) The theoretical amount of oxide that could be completely reduced by a given amount of aluminum with the resultant complete oxidation of the aluminum was determined. The chemical expression for a thermite reaction using Cr_2O_3 as an example may be written as follows:

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3 + Heat \qquad (1)$$
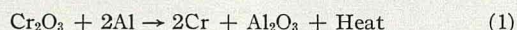
The chromium oxide, or other oxide that was reduced by aluminum, and the aluminum were considered as the reactants. The resulting chromium and other reduced metal and aluminum oxide were considered to be the reaction products. To control or throttle the reaction, any of the reaction products could be added to the thermite. Throughout this study, however, aluminum oxide was used as the control agent when required.

(2) This stoichiometric mixture together with the desired quantity of control agent was weighed out in an amount that would provide a pellet approximately $^5/_8$ in. long.

(3) 0.3 ml. of water was added and the materials were mixed thoroughly in an agate mortar and pestle.

(4) The mixture was transferred to the die used to form the pellet and was pressed with a total force of 2000 lb.

Throughout this study the aluminum used was the finest grade produced in commercial quantities by the Aluminum Company of America and was designated as 123 atomized aluminum powder. The particle size of this aluminum powder was 100% less than 45 μ with essentially no material less than 4 μ. The aluminum oxide used as a control agent was Alcoa −325-mesh A–3 calcined alumina. The reference pellet was of calcined kaolin pressed in a similar manner.

Early in this study it was noted that in many cases the pellet remaining after ignition retained its original shape and underwent only slight dimensional changes. Of further interest was the fact that the products of reaction were in effect a cermet. Although a similar method had been used to produce a cermet,[2] it was felt that this process represented a new approach. It therefore was decided that emphasis would be placed on evaluating the thermite reaction and its
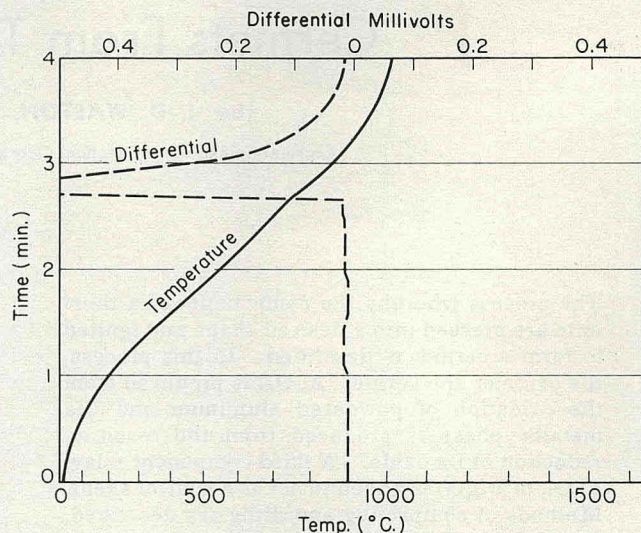
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[2] S. Krapf, "Process Using Heat of Reaction," *Ber. deut. keram. Ges.*, **31** [1] 18–21 (1954); *Ceram. Abstr.*, **1954**, July, p. 126*h*.

Fig. 2. Plot of differential thermal analysis data showing reaction of 25% Al_2O_3 and 75% Co_3O_4 thermite pellet.

Table I. Oxides Used to Produce Cermets

Oxide	Equivalent free energy of formation at 25°C. (kcal./mole of O)	Ref. temp. at ignition (°F.)	Thermite to produce fusion (%)	Differential mv.
Al_2O_3	−125.59			
Co_3O_4	− 51.0	1725	50	+1.70
Cr_2O_3	− 83.3	1620	80	+5.0
Fe_2O_3	− 59.0	1800	60	+5.0
MnO_2	− 55.7	1670	60	+2.74
MoO_3	−60.11	1040	70	+5.0
NiO	− 51.7	1580	70	+5.0
SiO_2	− 96.2	1470	100	+5.0
TiO_2	−101.9	1635	70	+5.0*
V_2O_5	− 69.0	1260	70	+5.0
ZrO_2	−122.2	1580	90	+5.0*

* No fusion.

products from the standpoint of producing a cermet, rather than merely using the heat produced to melt a coating material.

III. Results

Figure 2 is a reproduction of the data recorded using the differential thermal analysis equipment when a 75% cobaltous-cobaltic oxide (Co_3O_4) thermite and 25% aluminum oxide pellet was heated as described.

Figures 3 and 4 show a magnified cross section of two chromium oxide thermite pellets after ignition. Figure 3 is a 50-50 thermite and aluminum oxide composition, and Fig. 4 is a 75% thermite and 25% aluminum oxide composition.

Table I lists the oxides used to form such thermites with aluminum, and shows the temperature at which ignition took place, the amount of thermite required to produce fusion of the pellet as shown in Fig. 4, and the differential millivolts recorded between the reference pellet and the thermite pellet at the peak of the reaction. Compositions of thermite and inert aluminum oxide were investigated only at 10% intervals. All firing was done in air.

Fig. 3.   Cross section of 50% Al_2O_3 and 50% Cr_2O_3 thermite pellet.
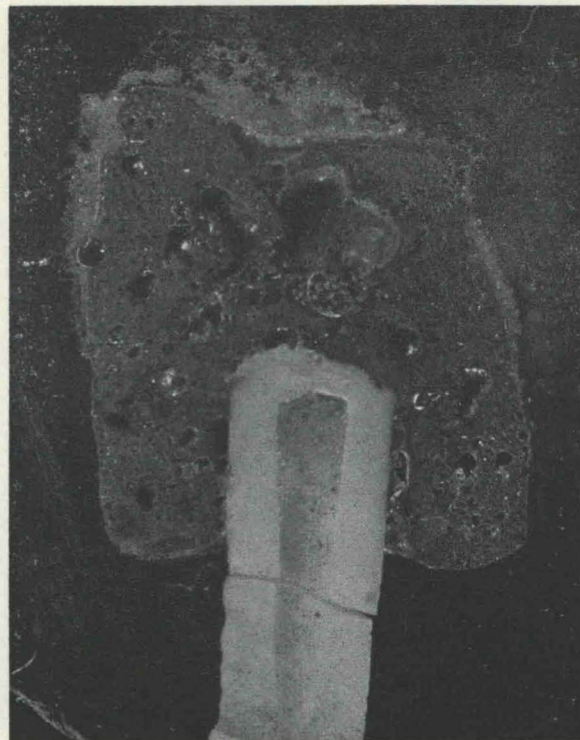

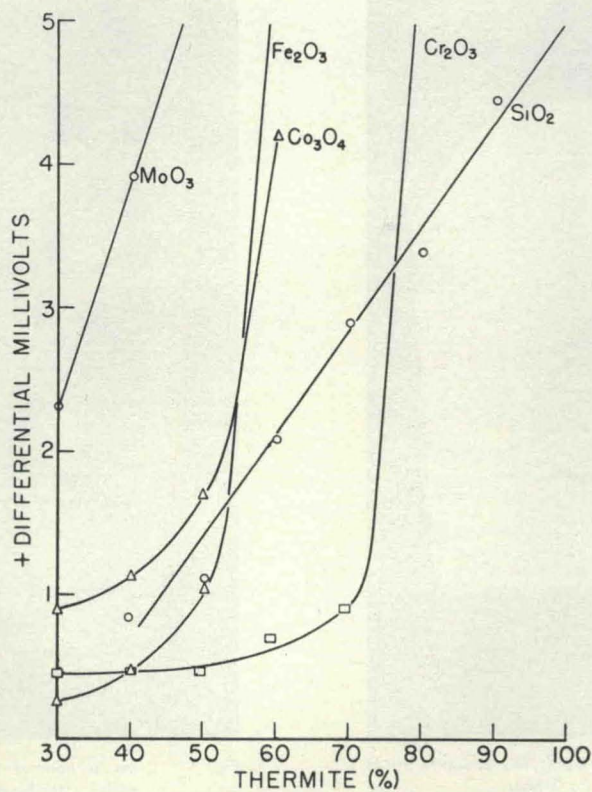Fig. 4.   Cross section of 25% Al_2O_3 and 75% Cr_2O_3 thermite pellet.

Fig. 5.   Per cent thermite vs. differential millivolts at peak of ther-
mite reaction for five oxides.

Complete data of differential millivolts versus percentage thermite for a few of the oxides studied are presented in Fig. 5.

Figures 6 and 7 show a 50% titanium dioxide (TiO_2) thermite and 50% aluminum oxide pellet.   Figure 6 shows a cross section of the pellet as it appeared after immediate
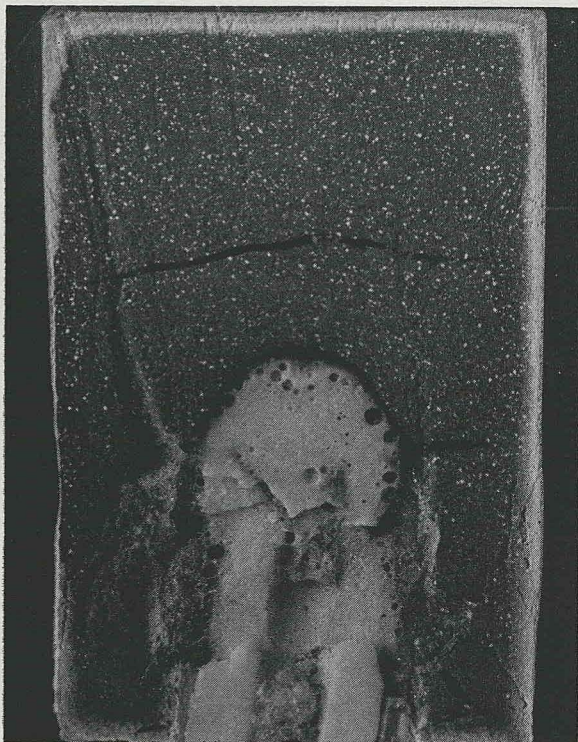
Fig. 6.   Cross section of 50% Al_2O_3 and 50% TiO_2 thermite pellet.
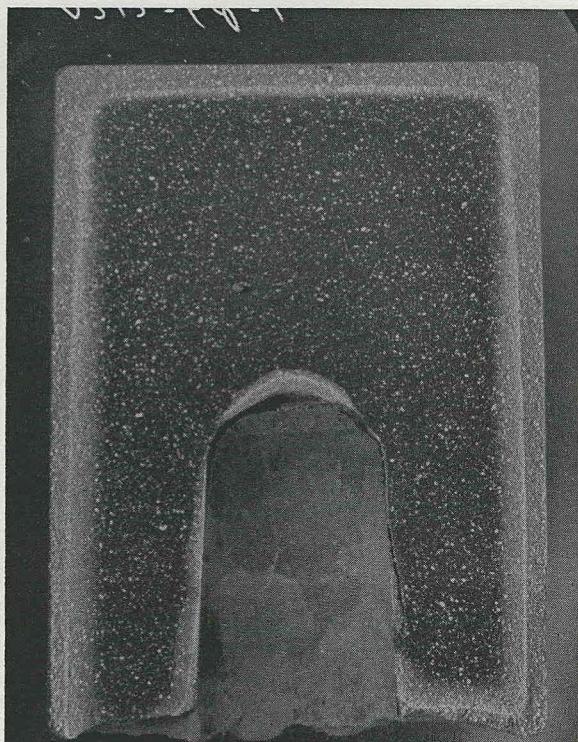
Fig. 8.   Cross section of 50% Al_2O_3 and 50% ZrO_2 thermite pellet.

Fig. 7.   Cross section of 50% Al_2O_3 and 50% TiO_2 thermite pellet after heating to 2500°F. for 3 hours.

Fig. 9.   Cross section of 50% Al_2O_3 and 50% ZrO_2 thermite pellet after heating to 2500°F. for 3 hours.

removal from the furnace after the thermite reaction had ceased. Figure 7 shows a duplicate ignited pellet after reheating at 2500°F. for 3 hours.

Figures 8 and 9 show pellets that were treated identically to those shown in Figs. 6 and 7 except that the oxide used was zirconium dioxide rather than titanium dioxide.

Fig. 10.   Cross section of 50% Al$_2$O$_3$ and 50% ZrSiO$_4$ thermite pellet.

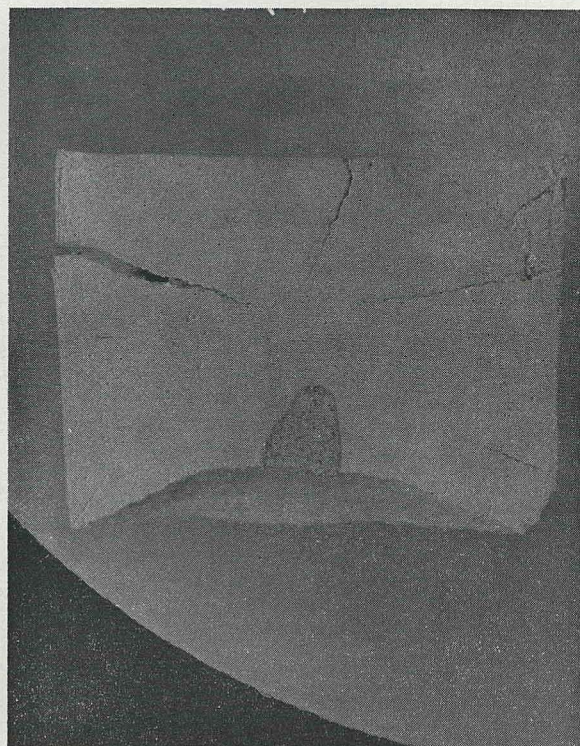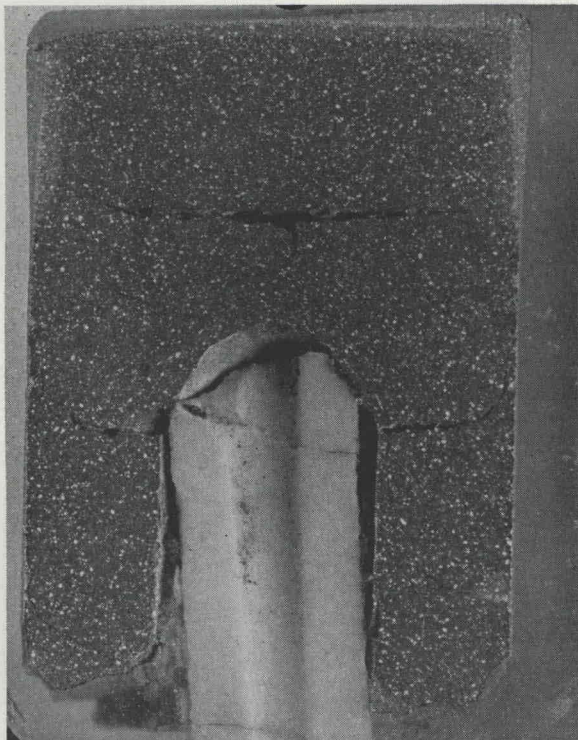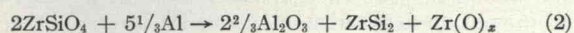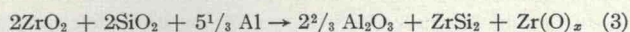Fig. 11.   Cross section of 50% Al$_2$O$_3$ and 50% ZrSiO$_4$ thermite pellet after heating to 2500°F. for 3 hours.

To obtain data on mixed-oxide thermites, a zirconium silicate thermite pellet was prepared and ignited. Figures 10 and 11 show the 50% thermite and 50% aluminum oxide pellets after ignition and reheating to 2500°F. for 3 hours. An X-ray analysis of the ignited zirconium silicate thermite revealed that zirconium disilicide was a major reaction product. Figure 12 presents the X-ray data obtained for a 100% zirconium silicate thermite after ignition.
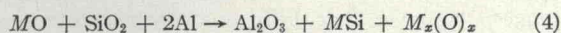
A thermite was prepared from equal mole parts of zirconium dioxide and silicon dioxide with the aluminum required for complete reduction. This thermite was mixed with equal parts of aluminum oxide to produce as nearly as possible the chemical equivalent of the zirconium silicate thermite shown in Figs. 10 and 11. This thermite, after ignition, provided the same products of reaction as the zirconium silicate thermite. The reactions thus observed could be expressed as

$$2ZrSiO_4 + 5^1/_3Al \rightarrow 2^2/_3Al_2O_3 + ZrSi_2 + Zr(O)_x \quad (2)$$

or

$$2ZrO_2 + 2SiO_2 + 5^1/_3 Al \rightarrow 2^2/_3 Al_2O_3 + ZrSi_2 + Zr(O)_x \quad (3)$$

or generally as

$$MO + SiO_2 + 2Al \rightarrow Al_2O_3 + MSi + M_x(O)_x \quad (4)$$

where M represents the metal whose silicide is to be formed.

Inasmuch as this method is a means of producing a silicide, it was decided that the same technique would be investigated as a means of producing a boride. Titanium oxide and boron oxide (B$_2$O$_3$), in the proportions represented by the expression

$$TiO_2 + B_2O_3 + 3^1/_3Al \rightarrow TiB_2 + 1^2/_3Al_2O_3 \quad (5)$$
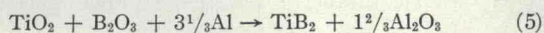
were selected to produce titanium diboride (TiB$_2$). X-ray analysis of the products of the foregoing reaction revealed that essentially all the titanium had been converted into titanium diboride.

The formation of carbides was the next attempt to create intermetallic compounds. The materials used and the proportions selected are shown in the following:

$$TiO_2 + C + 1^1/_3Al \rightarrow TiC + ^2/_3Al_2O_3 \quad (6)$$

$$SiO_2 + C + 1^1/_3Al \rightarrow SiC + ^2/_3Al_2O_3 \quad (7)$$
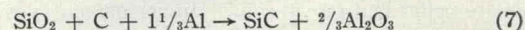
X-ray data verified the fact that under conditions afforded by the thermite reaction, essentially all the titanium and silicon produced combined with the carbon to form the respective carbide. Figure 13 presents the X-ray data obtained for the ignition products of the titanium dioxide and carbon thermite pellet.

IV.   Discussion of Results

From Fig. 2 it can be seen that the differential thermal analysis using the pellet method of specimen preparation provided a very rapid means of determining the temperature at which the reaction began as well as a measure of the intensity and duration of the reaction. As it was necessary to keep the thermite from direct contact with the thermocouple, an absolute reading of the thermite reaction temperature was not possible. However, for the purpose of this evaluation study, relative values were assumed to be sufficient.

The amount of control agent used determined the characteristics of the pellets, which ranged from the slightly sintered structure shown in Fig. 3 to the fused, bloated condition exhibited by the pellet in Fig. 4.

The curves shown in Fig. 5 are those obtained for a few of the oxides studied. These curves seem to fall into two categories, the type shown by the silicon dioxide and molybdenum trioxide (MoO$_3$) curves and the type represented by the other oxides. The relation between the heat produced by the reaction and the percentage of thermite used was linear over the range studied for silicon dioxide and molybdenum trioxide thermites. Although only two points are shown for the MoO$_3$ thermite curve, it should be mentioned
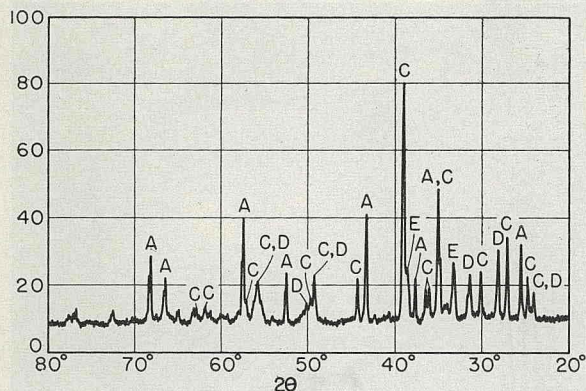
Fig. 12. X-ray diffraction pattern of 100% ZrSiO₄ thermite pellet after ignition. $A = Al_2O_3$, $C = ZrSi_2$, $D = ZrO_2$, and $E = ZrN$ or ZrO. Peaks designated ZrN or ZrO correspond to a NaCl-type lattice with cell edge of about 4.64 a.u. Pattern was obtained with a North American Philips diffractometer using copper radiation filtered through nickel foil.
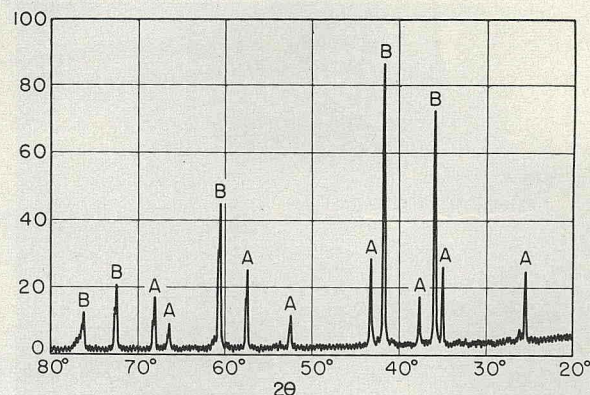
Fig. 13. X-ray diffraction pattern of 100% TiO₂ carbon thermite pellet after ignition. $A = Al_2O_3$ and $B = TiC$. Pattern was obtained as indicated in Fig. 12.

that the 50% thermite ignition produced a maximum differential slightly in excess of 5 mv. for only a matter of 1 or 2 seconds. For the other thermites, however, there appeared to be a point at which the rate of reaction proceeded with extreme vigor as the percentage of thermite was increased. No attempt was made to have all oxides of the same particle size, and this variable may have influenced the results obtained.

When the titanium dioxide thermite was removed from the furnace and the cross section of the pellet was examined, it was evident that the outer portion of the pellet had reoxidized (Fig. 6). A second pellet therefore was reheated to 2500°F. for 3 hours after ignition (Fig. 7). Examination of a cross section of this pellet revealed that essentially the entire pellet had reoxidized. Higher percentages of thermite were not studied; it may be, however, that a denser structure could be produced under different conditions and that a composition less subject to oxidation could be developed.

Figures 8 and 9 show that the zirconium dioxide thermite behaved in a manner similar to the titanium dioxide thermite.

By properly designing a thermite containing either zirconium or titanium dioxide, a cermet containing either zirconium or titanium with aluminum oxide should be made oxidation resistant or at least made to form a protective oxide layer that would prevent further oxidation. A condition similar to this apparently was obtained when a thermite pellet containing zirconium silicate as the oxidant was prepared and fired (Fig. 10). Upon reheating to 2500°F. for 3 hours it was found that only the outer surfaces were oxidized. As can be seen from Fig. 11, the interior of the pellet was oxidized only where there were previous cracks. This would appear to be a case where a self-healing protective oxide layer was formed.

X-ray analysis of the reaction products revealed that zirconium disilicide was produced as shown in reaction (2). The products were identified by comparing the observed patterns with data in the A.S.T.M. Index of Powder Diffraction Data. An attempt to form the same products from zirconium dioxide and silicon dioxide as shown in reaction (3) proved to be successful. It was also interesting to note that when the zirconium dioxide:silicon dioxide mole ratio was changed to provide an excess of either silicon dioxide or zirconium dioxide, the product zirconium disilicide was always formed.

A boride of titanium was similarly produced as indicated by reaction (5). In this instance only the mole ratio (titanium dioxide:boron oxide) of 1:1 was used. The interior

structure produced by this thermite was very dense and metallic with an extremely rough striated outer surface. However, only the pure thermite was used; no control agent (such as aluminum oxide) was added.

Carbides of titanium and silicon were produced according to reactions (6) and (7). The carbon was added as carbon black. The type used was Witcoblak Hitone, manufactured by the Witco Chemical Company. All three components, oxide, carbon, and aluminum, were hand mixed in an agate mortar and pestle and charged into the mold for pressing. From the results obtained it appeared that any desired carbide could be thus formed and used in combination with the aluminum oxide to develop new cermets. No aluminum carbide was formed and there was only the very weakest evidence that there was any original oxide or resulting uncombined metal in the final product. Thus, in only a matter of a few seconds, at the high temperatures developed by the thermite, the reaction between the metal and carbon took place to form the desired carbide.

For all the oxides used as constituents in the thermites studied, exothermic reactions were observed for some combination of thermite and inert Al₂O₃. Thus, by the use of aluminum powder, all the oxides underwent some degree of reduction, as determined by X-ray analysis.

On the basis of the equivalent free energies of formation for the oxides listed in Table I, ZrO₂ and TiO₂ would be the two oxides least likely to be reduced by aluminum. The X-ray data for the thermites containing only these oxides and aluminum showed that the metals were either absent or present in only minute quantities after ignition. The high susceptibility of these metals to oxidation at elevated temperatures, and the fact that the ignition was carried out in air, would preclude the presence of the unoxidized metal for any appreciable length of time after ignition. The formation of zirconium disilicide and titanium carbide suggests, however, that the metals may have been completely reduced in order to react with the silicon and carbon, respectively, thus forming the more oxidation-resistant intermetallic compounds observed in Figs. 12 and 13.

As a later experiment to establish whether or not aluminum had the ability to reduce TiO₂, a thermite specimen was prepared that may have reacted according to the following:

$$TiO_2 \text{ (rutile)} + 1\tfrac{1}{3} Al \rightarrow \tfrac{2}{3} Al_2O_3 + Ti \qquad (8)$$
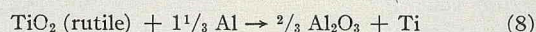
This specimen was fired and cooled in an argon atmosphere, and the following conclusions were reached from an X-ray analysis of the reaction products:

Except for the presence of a line at 2.21 a.u., it could be said that the crystalline portion of the specimen consisted

almost entirely of alumina and titanium, the titanium being in very small crystallites or severely strained, as shown by the broadened shape of the diffraction lines. Efforts were made to check for the presence of the following materials and it is believed that they were not present: β-titanium, TiO (low form), (TiO), TiO_2 (rutile, anatase, brookite), α-Ti_2O_3, α-$Al_2O_3 \cdot TiO_2$, β-$Al_2O_3 \cdot TiO_2$, Al_3Ti, and AlTi. The structure and X-ray diffraction patterns of the high-temperature forms of TiO and Ti_2O_3 were not known.

The effect of aluminum particle size was examined briefly by preparing some of the thermite mixtures using Alcoa No. 140 atomized aluminum powder. This aluminum powder was 100% less than 30 μ and 10% less than 3 μ. The thermites prepared using this powder attained the desired temperatures of reaction and degree of fusion with from 5 to 15% less thermite than that required when the coarser 123 powder was used.

Clay was thought to be a desirable control agent, as its plasticity would lend itself to lubrication during pressing and perhaps reduce the forming cracks evidenced in many of the thermites after ignition. Because clay contains silica that probably would be reduced during the reaction, a test pellet was made of clay and the amount of aluminum required theoretically to reduce the silica in the clay. This mixture did produce a thermite with the resultant reduction of the silica to silicon. Thus, when clay is used as a control agent, it must be taken into account that the silica will enter into the reaction, producing silicon in the final cermet.

The use of clay, however, provided a useful addition to facilitate the testing of the possibility of slip casting a thermite mixture. A suspension of 80% zirconium silicate thermite and 20% of a 50-50 mixture of ball clay and kaolin was prepared. This slip was used to cast a small tapered cylindrical shell in a plaster mold. The piece was dried and heated to the ignition temperature of the thermite. This experiment indicated that slip casting could be used as a means of forming thermite shapes to produce the desired cermets. The density and general appearance of the cermet thus formed was very similar to that produced when the ingredients were pressed into the form of a pellet and ignited.

For a better description of a cermet formed from such a thermite reaction, it is suggested that the term "thermitic cermet" be used.

V. Preparation of Thermitic Cermet Test Specimens

Inasmuch as it was learned from the preliminary studies of this project that a cermet could be formed from a thermite reaction, it was felt that a detailed study should be made of a single basic thermite mixture. The zirconium silicate thermite (reaction (2)) was selected for this study because it exhibited the following characteristics:

(1) It formed a cermet that was an intermetallic compound and aluminum oxide.

(2) It formed a cermet that had the ability to form a self-healing protective oxide layer.

(3) It formed a dense, strong cermet.

(4) Its reaction could be easily controlled over a wide range of inert additions.

(5) It did not lend itself to easy formation of desired shapes by conventional powder metallurgical techniques. Thus, it was felt that if forming difficulties could be overcome using these components, then most of the forming difficulties could be eliminated when other thermite mixtures were used.

The basic mixture was composed of stoichiometric proportions of zirconium silicate and aluminum. Clay was introduced into the mixture as a reaction throttler. It was used in preference to aluminum oxide for its plasticity and effect of increasing the strength of the resulting cermet.

In the preliminary studies Alcoa No. 140 atomized aluminum was used as the reductant in the thermite mixture and TAM Superpax (zirconium silicate)* was used as the
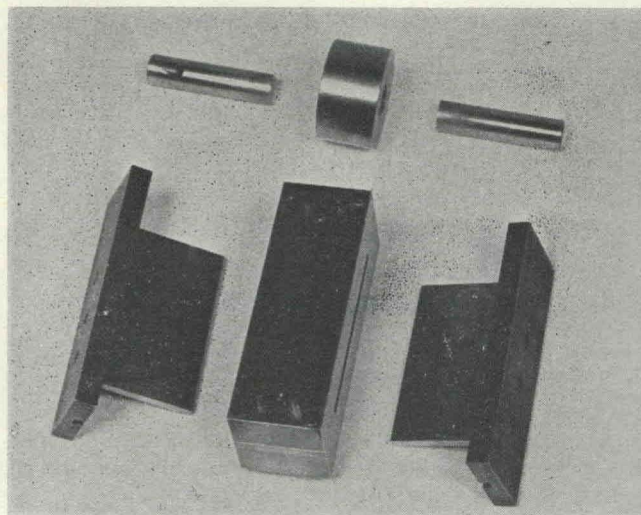

Fig. 14. Dies for compacting thermitic cermets.

oxidant. Particle-size studies indicated that these two materials had particle-size distributions that would produce an optimum reaction of the thermite and thus produce a strong cermet. The particle size of the powdered aluminum was found to have a normal distribution of between 2 to 15 μ and the particle size of the zirconium silicate to have an average particle size of 5 μ with an upper limit of 10 μ. Inasmuch as Alcoa No. 140 atomized aluminum could be obtained only in small quantities for laboratory use, there was a need for substituting a commercially available aluminum. It was felt that this substitution could be accomplished by milling. The powdered aluminum that was used in these studies was Alcoa No. 123 atomized aluminum, which was found to have a distribution between 4 and 44 μ.

(1) Milling

The mill charge was composed of stoichiometric proportions of zirconium silicate and aluminum. EPK clay was included in the charge as the control agent and lubricant. A 500-gm. charge was composed of 304 gm. of zirconium silicate, 121 gm. of aluminum powder, and 75 gm. of EPK clay. These components were charged into a $\frac{1}{2}$-gallon steel mill with 4650 gm. of $\frac{9}{16}$-in.-diameter steel balls and 650 ml. of toluene. The mill was then allowed to roll at 72 r.p.m. for 8 hours.

(2) Drying

The toluene tended to form a very small quantity of an organic resin that coated the thermite particles. However, the following method of removing this resin was developed: The mill was dumped into a shallow pan, the thermite mixture was allowed to settle, and the excess toluene was decanted off. Next, the thermite mixture was dried slowly at 40° to 50°C. in a well-ventilated hood. The dried thermite mixture was then heated to 800°F. for 30 minutes. This temperature and time was sufficient to remove any resins that may have been formed from the toluene.

(3) Compacting

(A) *Apparatus:* Two basic die designs were used; these are shown in Fig. 14. The cylindrical die was used to form tablets $\frac{3}{4}$ in. in diameter. This die was used in preliminary

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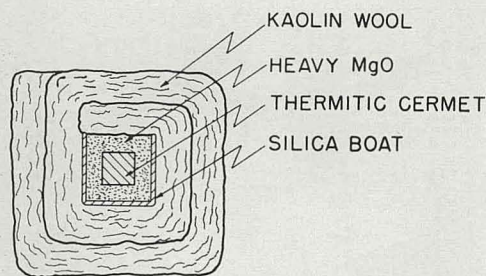
Fig. 15. Dual shrouding for firing thermitic cermets.

Fig. 16. High-temperature testing apparatus.

work to determine whether the thermite mixture prepared in one way or another would ignite and to determine its general appearance and structure after ignition.

The bar die was used to compact a 4- by $1/4$- by $1/4$-in. bar that was used to obtain the strengths of the thermitic cermets. It was constructed from tool steel that was hardened to a Rockwell hardness of 59. The clearance between the plunger and the die cavity was held to 0.0005 in. This clearance was necessary to prevent excess material flow past the plungers.

(B) *Specimen Preparation:* (i) *Lubricant:* The specimens were dry pressed using a saturated solution of Al(OH)$_3$ as the lubricant. Other lubricants that could act as binders were also investigated. These included such organic resins and compounds as Abitol, anthracene, melamine resin 248–8, phenolic Bakelite plastic, P–354–50 Beckamine urea formaldehyde, Nos. 4000 and 6000 Carbowax, and stearic acid. None of these resins proved to be superior to the saturated aqueous solution of Al(OH)$_3$. They were difficult to remove from the thermitic compacts and in some cases prevented the thermite reaction from taking place.

(ii) *Pressing:* Two pressing techniques were investigated. They were progressive and single-step pressing. Progressive pressing is a press and release, re-press and release; i.e., if a compacting pressure of 10 tons per sq. in. is desired, a pressure of 2.5 tons per sq. in. is applied and released; then 5 tons per sq. in. is applied and released; then 7.5 tons per sq. in., etc. Single-step pressing is simply the application of the desired pressure in a single press and release. The use of progressive pressing was an attempt to expel air entrapped in the compact. As will be shown later, no conclusive evidence was obtained to indicate that progressive pressing was the better technique; it appeared, however, to have some merit.

(iii) *Forming of Thermitic Cermet Bars:* Ten grams of the prepared thermite mixture was milled with a selected volume, which should not exceed 2 ml. of the saturated aqueous solution of Al(OH)$_3$, in a mortar and pestle. This mixture was then placed into the cavity of the 4- by $1/4$- by $1/4$- in. bar die that had one of its plungers inserted approximately one-third of the way in. The mixture was lightly tamped so that it would be evenly distributed in the cavity. The top plunger was then inserted into the die and pressure was applied to both of the plungers. After the desired pressure had been applied and removed, the bar was removed from the die and dried at 110°C. The dried bar was then fired.

(iv) *Firing:* The most satisfactory method of firing the bars to date is by dual shrouding; i.e., the bars are shrouded by a refractory powder that is in turn shrouded or incased in an insulating material. Figure 15 is a cross section of the assembly which illustrates the dual shrouding technique that was used. The bars were shrouded in powdered magnesium oxide (heavy) in a silica boat. An insulating material (kaolin wool) was then wrapped around the silica boat until a double layer was obtained. The kaolin wool was
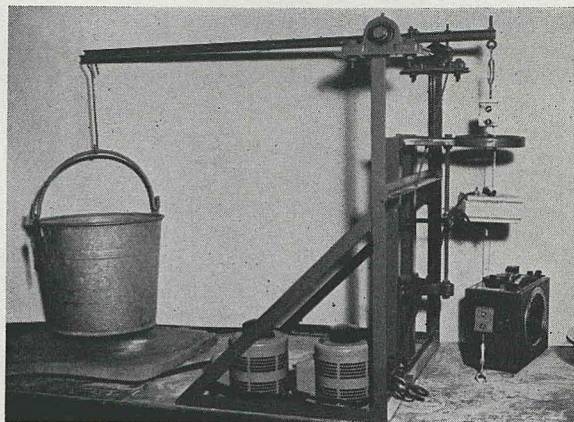
secured with Nichrome wire. The shrouded bars were then fired at 1800°F. for 1 hour. This period of time was found to be necessary for the ignition of the thermite to occur. The bars fired by this technique were superior to any of the bars fired by the other methods studied. They were very dense and exhibited a modulus of rupture of 18,200 lb. per sq. in.

(4) Physical Tests and Measurements

The transverse strengths or moduli of rupture of the test bars were obtained using a Dillon Universal Tester having a maximum applied load of 1000 lb.

The high-temperature tensile strength was determined using the apparatus shown in Fig. 16. A simple lever was used to apply a load to the heated test bar. The test bar was heated with a Kanthal-wound furnace and temperatures were measured with a Chromel-Alumel thermocouple located near the center of the test bar. The load was gradually applied to the test bar by pouring sand into the bucket suspended at the other end of the lever.

Conventional tensile testing grippers could not be used on a fired thermitic cermet bar. Because of its extreme hardness, the bar slipped out of the jaws of the grippers. To overcome this difficulty, three holes were drilled in the bar before it was fired. A $7/64$-in. hole was drilled $1/2$ in. from each end. Inconel wire was threaded through the holes and in turn was attached to the lever and test bed by turnbuckles. The purpose of the turnbuckles was to maintain the lever in a horizontal position. A $9/64$-in. hole was drilled in the center of the bar to decrease the cross-sectional area of the bar, similar to the necking-down of specimens for conventional tensile testing. The bar was suspended through the center of a small muffle furnace. One inch of the center of the bar was heated by the furnace to the testing temperature and a uniform increasing load was applied to the bar until it failed. The point of failure occurred at the center of the bar where its cross-sectional area was the smallest. Values in excess of 5000 lb. per sq. in. were obtained for the basic thermitic cermet at both 84° and 2200°F. This test equipment is being rebuilt to provide higher test temperatures, as no effect of temperature on the tensile strength of these cermets could be determined up to 2200°F.

(5) Compositional Studies

These studies were made by adding the oxides of chromium, cobalt, manganese, and nickel to the basic zirconium silicate thermite mixture in an attempt to increase the ductility of the thermitic cermets. Thermite mixtures of zirconium silicate and those of the oxides listed were milled wet for a period of 8 hours. Alcoa A–3 alumina and thermite mixtures of the oxides mentioned were added to the zirconium silicate
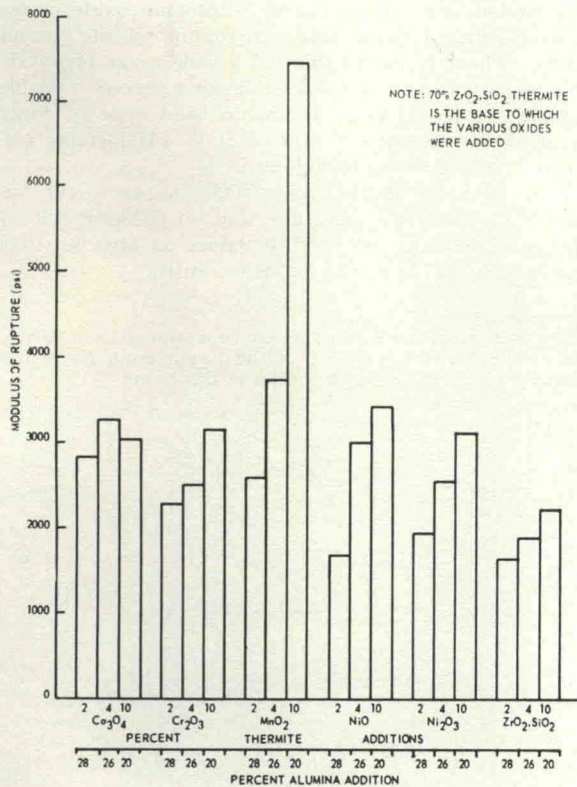
Fig. 17. Effect of various oxide additions on strength of thermitic cermets.

Fig. 18. Metallograph of fired thermitic cermet (×12).

thermite mixture in varying proportions. Thermitic cermet bars were prepared from these compositional mixtures using a compacting pressure of 10 tons per sq. in. Figure 17 is a bar graph that shows the effect of the oxide additions on the fired modulus of rupture of the thermitic cermets.

The transverse strength of the fired zirconium silicate thermitic cermets was improved by the addition of other metals. The manganese dioxide thermite addition to the basic zirconium silicate mixture produced the strongest bar.

Studies were made to determine the effect on the transverse strength of the thermitic cermet bars of the compacting pressure, method of applying the pressure, and the quantity of lubricant used. Table II lists the effect of these three variables on the fired transverse strength of the basic thermitic cermet bars (85% zirconium silicate thermite and 15% EPK clay).

The ideal ignition of the thermitic cermet bars occurred when the ignition started at one end of the bar and proceeded to the other end. Ignition sometimes occurred at both ends of the bar, and when these two burning lines met, a necking-down of the bar resulted from the excess heat produced. Whenever this occurred, the bars were not tested for their transverse strengths, as the bars would break at the necked-down section, giving unreliable results. Therefore, no values are listed in Table II for the bars that ignited in this manner.

Although most of the transverse strengths appeared to be inconsistent, the strengths of the bars compacted using 5 and 7.5 tons per sq. in. appeared to be the most consistent in the progressive pressing, and 5 tons per sq. in. in the single pressing. The progressive pressing produced more bars that ignited ideally. The quantity of lubrication added in the bars compacted by progressive pressing at 5 and 7.5 tons per sq. in. and by single pressing at 2.5 tons per sq. in. resulted in a noticeable trend.

Figure 18 is a metallograph of a fired thermitic cermet bar. The white particles are aluminum oxide. It can be seen that the particles do not cluster. It was observed that when the aluminum oxide particles tended to cluster, the bar exhibited low transverse strength.

The crack beginning at the corner of the bar is an internal stress crack that formed during the compacting operation and was subsequently enlarged by firing. These internal stress cracks have been eliminated by using lower compacting pressures.

VI. Conclusions

Cermets can be preformed from a thermite composition according to the following reaction:

$$MO + Al \rightarrow M + Al_2O_3 + \text{Heat} + M_x(O)_x \qquad (9)$$
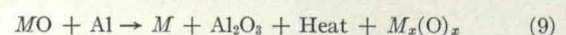
where M represents a metal whose oxide has a free energy of formation (per equivalent) less than that of aluminum oxide.

Cermets containing intermetallic compounds as the metallic phase may be formed by this technique. The general equation for forming silicides may be stated as

$$\left.\begin{array}{c} MO \cdot SiO_2 \\ \text{or} \\ MO + SiO_2 \end{array}\right\} + Al \rightarrow MSi + Al_2O_3 + \text{Heat} + M_x(O)_x \qquad (10)$$

Table II. Effect of Lubricant Addition, Compacting Pressure, and Method of Compacting on Fired Transverse Strengths of a Zirconium Disilicide and Aluminum Oxide Cermet

	Lubricant (ml.)*	Transverse strength (lb./sq.in.) under a compacting pressure of			
		2.5 tons/ sq. in.	5.0 tons/ sq. in.	7.5 tons/ sq. in.	10.0 tons/ sq. in.
Progressive pressing	0.67	16,590	13,990	7,985	16,110
	1.00	12,900	11,560	9,650	13,075
	1.33	11,840	18,350	11,000	13,050
	1.67	9,000	16,250	19,190	
	2.00	18,265	13,625	16,425	
Single-step pressing	0.67	5,890	14,840	9,680	
	1.00	7,970	18,685	15,015	
	1.33	9,540	17,875	18,570	
	1.67	11,050	15,140		
	2.00	16,210	19,470	10,930	

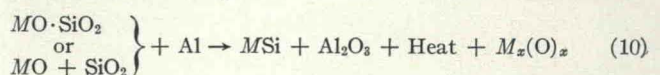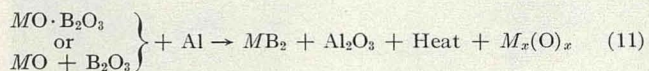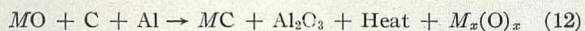* The lubricant used was a saturated aqueous solution of Al(OH)₂.

for borides,

$$\left.\begin{array}{c} MO \cdot B_2O_3 \\ \text{or} \\ MO + B_2O_3 \end{array}\right\} + Al \rightarrow MB_2 + Al_2O_3 + \text{Heat} + M_x(O)_x \quad (11)$$

and for carbides,

$$MO + C + Al \rightarrow MC + Al_2O_3 + \text{Heat} + M_x(O)_x \quad (12)$$

Although such cermets are only in the early stages of evaluation, the following apparent potentialities make further investigation desirable: (1) inexpensive compositions, (2) low temperature of ignition (1800°F.), (3) high reaction temperatures (+5000°F.), (4) short firing time, and (5) controlled atmosphere not necessary in all cases.

Self-bonded zirconium disilicide-aluminum oxide cermets were successfully formed from a zirconium silicate thermite mixture. These cermets exhibited a wide range of physical properties that depended on the following process variables: (1) material preparation, (2) amount and type of control agent used, (3) presence of other metals, (4) forming technique used, and (5) firing technique used.

Tensile strengths in the range 5000 lb. per sq. in. were obtained at room temperature and at 2200°F. Room-temperature modulus of rupture values as high as 19,000 lb. per sq. in. were obtained from such cermets.