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CEMENTITIOUS CERAMIC MATERIALS

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PICATINNY ARSENAL
DOVER, NEW JERSEY

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Picatinny Arsenal Technical Memorandum 1204

CEMENTITIOUS CERAMIC MATERIALS

by

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ABSTRACT

A brief study of the chemistry of cementitious, or "air setting," ceramic materials for protective coating and potting applications is presented. Included are the three main types of bonding mechanisms -- reaction, precipitation, and hydraulic. Fillers which can be incorporated into the compound, as well as other physical and chemical characteristics of the materials, are considered.

There are commercially available materials which are useful to about 3000° F. These compounds, which utilize different types of bonding with various fillers, are discussed and compared. Several of the materials have been used successfully at Picatinny Arsenal in munition applications, such as coatings for rocket components and shaped charge cones.

Two Air Force sponsored research programs deal with cementitious materials. The first is an attempt to develop inorganic air-setting adhesives for use to 1000° F. Results of this project indicated that shear values of 800 psi at room temperature and 1600 psi at 800° F may be expected. The second program, the development of a coating for thermal protection of structures to 3500° F, resulted in two promising acid-bonded oxide compositions.

INTRODUCTION

Because of the increasing demands being placed on our weapon systems, greater emphasis is now being directed toward development of new and improved materials. Since materials are required which have greater thermal stability, improved structural properties, and better electrical and magnetic properties, an increased effort in the investigation of ceramic materials has resulted.

One category of ceramic materials which has potential for applications in munition commodities is cementitious ceramic materials. The important advantage of these materials, which have not yet been given extensive consideration, is that they do not require the high temperatures normally necessary in ceramic fabrication. These cements develop their final properties at temperatures seldom in excess of 500° F.

Cementitious, or "air setting," ceramic materials are ideally suited for protective coatings and encapsulation agents, and, to a lesser degree, as high temperature adhesives. Present organic sealants, encapsulating agents, and adhesive compounds can not withstand temperatures above 900° F. However, ceramic cements are useful to about 4000° F.

Cementitious ceramic materials can be used as inert encapsulates for both thermal and electrical insulation. As coatings they provide thermal insulation and protection against oxidation and erosion. These materials have been used successfully as coatings to protect rocket components such as igniter traps, propellant rods, and baffles; as seals between nozzle and insert; and as "potting compounds" for thermal batteries.

A cement is composed of a bonding agent and an aggregate, or filler. The end product is usually formed by a reaction of the bonding agent and the aggregate; the bonding material, although present in minor proportions, provides the strength for the system. The aggregate is often a refractory oxide, though it may well be a silicate, aluminate, or other ceramic. The mechanism of bonding is one or a combination of the following types:

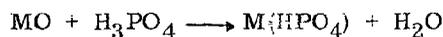
1. Formation of a precipitate
2. Reaction
3. Hydraulic action

This report reviews the more important aspects of the chemistry of cementitious materials and some of the more recent research and development programs. Commercially available materials are also discussed.

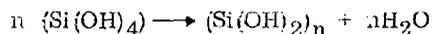
CHEMISTRY OF CEMENTITIOUS CERAMIC MATERIALS

There are three main bonding mechanisms which are of primary interest in cementitious ceramics (Ref 1).

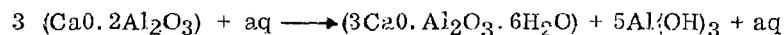
1. Reaction



2. Precipitation



3. Hydraulic



Reaction-type bonding includes the oxyphosphates, the air-setting acid phosphates, and the phosphoric acid bond in alumina. Other acid salts that can be used as bonding agents include nitrates and sulfates. "Oxy" bonds such as oxychloride are in this category, along with such bonds formed under artificial conditions as basic carbonate and hydrous calcium silicate.

A precipitation bond consists essentially of a gel, thrown out of colloidal dispersion by adjustment of acidity or ion concentration. The most familiar of the precipitation bonding agents are the alkali silicates; however, other silicates and esters can be considered to bond in this manner.

Hydraulic bonding involves the formation of a cement both by reaction with water and by precipitation. The characteristic that distinguishes hydraulic bonding from other bonding mechanisms is that hydraulic cements are only slightly soluble in water, but will react with it. Portland cements and calcium aluminates are the most common and useful hydraulic cements.

Two primary properties of interest when developing or investigating cementitious materials are cohesion and adhesion. The mechanism whereby

molecules or atoms in homogeneous matter are held together is known as cohesion, it may be due to chemical attraction, polarization, or attraction through van der Waals forces (Ref 2).

These forces, with different degrees of magnitude, are responsible for the cohesion between ions, atoms, and molecules of all forms of matter. Points of strength and weakness within a material can be ascribed to the presence of cohesive forces. The net effects of these forces determine the gross mechanical properties of all materials.

Cohesion is characteristic in any continuous body, but for a successful cement three-dimensional, isotropic cohesion is required. For optimum strength and bonding of a cement, cohesion must be due primarily to atomic lattices that are continuous in all directions, rather than to the interlocking of crystals.

Adhesion is the mechanism by which molecules or atoms of homogeneous matter are held to other homogeneous matter. "Specific" adhesion, or adhesion due to molecular attractive forces, is the primary factor in bonding between any two materials (Ref 3). Mechanical adherence due to surface roughness can be discounted as a permanent basis for effective bonding.

Cohesive and adhesive properties of any cement are due to the type of atomic bonds and lattice formation present. In this respect both organic and inorganic (ceramic) adhesives are very similar. In organic adhesives, bonding is caused by formation of hydrogen bonds between polar groups and the adherend surface. The same effect is thought to be responsible for adherence of inorganic cementitious materials such as acid salts, gels, and hydrated salts, all of which contain hydrogen or hydroxyl bonds as part of their set structure. In addition, the major or aggregate portions of most cement compounds are the refractory oxides, which are especially suitable to the same kind of bonding.

As mentioned previously, a random crystal structure is much more desirable for cements than a highly ordered crystalline arrangement. This random structure is capable of infinite continuity in three dimensions. Also, impurity ions which would not normally join a highly ordered structure would not affect a random structure, and therefore exact stoichiometry is not required in random structures. An additional advantage of the random structure is that bonds are not highly directed, and different nuclei bond together with the same random pattern as the rest of the structure.

In addition to their similarity to organic cements, inorganic cementitious materials are similar in structure to glassy materials. If oxygen is substituted for other anions or if the cements are dehydrated, almost all are capable of forming glasses. In both cases there are strongly bonded polyhedrons which have some flexibility in arrangement. There would be no possibility of random structure if edges or faces of polyhedrons were shared, because the location of adjacent polyhedrons relative to one another would be fixed. All the polyhedrons, which are usually complex ions, that form cements are capable of bonding by hydrogen bonds, hydroxyl bonds, or occasionally water bonds.

Hydrogen bonds are the primary bonding mechanism in acid salts, which are the most common cementitious materials in the reaction bonded category. The strongest known O-H-O bonds occur in potassium dihydrogen phosphate, KH_2PO_4 . Phosphoric acid itself forms hydrogen-bond glasses. A hydrogen bond is essentially a bridge between two oxygen atoms whose valence is not satisfied by their associated cations. Each oxygen atom is bonded to the hydrogen ion by a valence bond of strength $(B)1/2$. The two oxygen ions are always in different polyhedrons, and the hydrogen bridge is the bond between polyhedrons.

Hydroxyl bonds exist because of the dipole character of the hydroxyl ion. The hydrogen ion associated with the oxygen ion acts as a positive pole. The hydroxyl ion may act either as a normal univalent anion or as a through-bonding device. Usually the hydroxyl ion acts according to the former case; in the latter case the hydroxyl ion receives three-half strength valence bonds and gives one half-strength valence bond to another ion, for a new valence of -1. When the hydroxyl ion is a through-bonding device, reasonably random structures are developed. In structures which are tetrahedrally coordinated, such as silica gels, hydroxyl bonds may be one of the connecting links between tetrahedrons. In such structures a reasonable number of cations of high coordination can be accommodated without causing ordering, thus making them good cements.

BONDING MECHANISMS

Reaction Bonding

There are a great many cementitious materials for which reaction bonding is the setting mechanism. One of the most important groups of the reaction-bonded cement series is the acid phosphates. The following acid phosphates, which may be monobasic or dibasic, are all more or less effective bonding agents: of aluminum, beryllium, cadmium, calcium,

copper, chromium, iron, lanthanum, lead, tin, thorium, vanadium, yttrium, zinc, and zirconium.

Oxide-phosphoric acid reactions at room temperature fall into three distinct groups. Acidic or chemically inert oxides do not react with phosphoric acid. Highly basic oxides react so violently with phosphoric acid that a porous, friable structure results. Many other oxides of a weakly basic or amphoteric nature react with phosphoric acid, but not all of these reactions result in bonding products. The considerable number of oxides reacting to form bonded products indicates that this is a general property of the hydrogen phosphates rather than of any one chemical compound.

Therefore, the requirements for a material to form an acid phosphate may be summarized as follows. The oxide must react with the acid at a rate compatible with organization of the reaction products to form a cohesive mass. High basicity, which is equivalent to weak cation oxygen bonds that allow the bond to be broken easier than a hydrogen-oxygen, limits the bond strength. This is due to lack of covalent bond character, a low positive charge, large ionic radius, and low electronegativity. For less basic materials a more amorphous or glassy structure can result, since strongly bonded polyhedra are held together with considerably weaker forces. This allows a somewhat variable and flexible structure to form, and the residual fields present and flexible nature of these materials provide additional adhesion for bonding action.

In addition to the chemical reactions of oxides with phosphoric acid, it has been found that bonds may be formed by the loss of water from phosphoric acid or acidic phosphoric solutions. The most interesting of these is monoaluminum phosphate, $\text{Al}(\text{H}_2\text{PO}_4)_3$. The best cementitious properties are obtained when the material is heated to about 500° F. to form a metaphosphate.

Other phosphate bonds are those with titania and silica. Titanium hydroxide will react with phosphoric acid to form the basic phosphate, TiOHPO_4 . Silica and siliceous materials will yield a bond believed to be silicyl metaphosphate, $\text{SiO}(\text{PO}_3)_2$. Additional cements which may be classified as reaction type include magnesium oxychloride ($\text{MgCl}_2 \cdot 3\text{Mg}(\text{OH})_2$), a weather-sensitive material, and basic magnesium carbonate, $\text{Mg}(\text{OH})(\text{CO}_3\text{H})$.

Precipitation Bonding

Precipitation cements depend for their cohesion upon polymer formation by anionic complexes of glass-forming elements. The cations are small, highly charged, and capable of co-ordinating tetrahedrally with either oxygen or hydroxyl ions. This polymerization is typified by materials like silica. Silica gel has about the same structure as silica glass, except for some very fine grained heterogeneity. In silica sols with particle sizes under 150-200 millimicrons, the formation of Si-O-Si bonds between particles holds them in fixed position relative to one another and thereby leads to a rigid network which is a gel (Ref 4).

Initially the particles are bonded together into chains, probably by hydrogen bonding. However, since the surface of particles of colloidal silica is composed of SiOH groups, condensation between silanol groups occurs when these particles come together and siloxane bonds are formed between the particles (Ref 5).

Sodium silicate gels are very similar to pure silica gels. One difference is that the former dehydrate and fuse at temperatures above 500° C, while pure silica gels crystallize to cristobalite. Silica gels are strong cementitious materials, but form very slowly and are not efficient bonding agents. Because of the close control of properties and performance which is possible, alkaline silicates, usually those of sodium, are the foremost of the precipitation cements.

There are three kinds of alkali silicate cements. These are air-setting, by formation of the gel from a sol; heat setting, by reaction with other materials at higher temperatures; and chemically setting. Silicate gel bonding by chemical setting is of most interest, because the shrinkage in this type of cement is characteristically lower than others. The chemically setting silicate cements are based on the more siliceous compounds, usually in the range from $\text{Na}_2\text{O}:2.5 \text{SiO}_2$ to $\text{Na}_2\text{O}:4\text{SiO}_2$ and $\text{K}_2\text{O}:3\text{SiO}_2$ to $\text{K}_2\text{O}:4\text{SiO}_2$.

The aggregate to be used with the cement may react with the silicate. The materials which will react include magnesia, calcium carbonate, calcium sulfate, zinc oxide, lead oxides and carbonates, and heavy metal salts. However, refractory oxides are the primary materials of significant value in developing a thermally insulating compound with sufficient body strength.

Other materials, such as chlorides and easily soluble salts may be used, but these reactions using these materials are rapid and difficult to control. Acid salts may generally be used as precipitants or gelling agents.

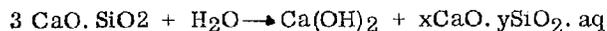
Sodium silicates are generally preferred over other silicates as the bonding medium because of availability and cost. However, potassium silicates are used for certain applications where specific electrical properties are required.

Chemically setting precipitated cements are considered better for applications where resistance to acids is required. These are usually based on silica, sodium silicofluoride, and sodium silicates with a higher ratio of silica than $\text{Na}_2\text{O} \cdot 3 \cdot 2\text{SiO}_2$.

Hydraulic

The principal types of hydraulic cements are portland, calcium aluminate, pozzuolanic, slag, natural lime-silica, barium silicate, and barium aluminate (Ref 6).

The process by which hydraulic cements set is known as hydration. Bonding compounds present in these cements are anhydrous, but when brought into contact with water they react, forming hydrated compounds. Supersaturated and unstable solutions are formed temporarily, but these gradually deposit their excess solids and tend to come into equilibrium with the hydrated compounds produced. This may be illustrated by the hydration of $3 \text{CaO} \cdot \text{SiO}_2$, which may be represented by:



The action of a hydraulic material when acting in a cementitious role can be summarized generally as follows. The cement grains are acted upon by water to form a supersaturated solution from which a gel-like mass of crystals precipitates. Diffusion of water molecules to the surface, or even into the crystal lattice, to react in-situ must also play a part in hydration. While still in a plastic condition the cement paste shrinks slightly because there is a contraction in volume of the system (cement and water) on hydration. Once the cement mass becomes rigid, a small expansion occurs due to the deposit of gel around the cement grains; the quantity of this mass increases with time and spreads into the inter-granular spaces. When the set cement is dried it undergoes an irreversible contraction and reduction in water content as the gel changes into a more stable form.

The ratio of water to cement is of great importance in hydraulic cements. It is a primary determinant of strength, since the strength of gels is inversely affected by the water retained upon setting. The strength of the cement increases as water content is decreased; however, there must be sufficient water for good workability, optimum compaction, and complete hydration.

The properties of hydraulic cement can be varied somewhat to meet the requirements for application. The primary applications for hydraulically setting cements have been as structural materials.

RATE OF REACTION AND SUBSEQUENT REACTIONS

There are two additional factors which bear on the effectiveness of a cementitious material. These are the rate at which the initial reaction proceeds, and the reactions occurring in the cement subsequent to hardening.

Rate of Reaction

The rate of reaction affects bond strength in that if the reaction occurs too rapidly, there is little chance for the necessary slight rearrangements in molecular structure which are needed for bonds to develop between adjacent particles. The rate of reaction depends both on the basicity of the cationic reactant and on the activity, or acidity, of the other reactants.

In acid phosphate bonding materials (reaction type), there is a close relationship between rate of reaction and cementitious behavior. Slightly basic elements form good bonds by direct reaction of their active oxides with phosphoric acid. The more basic elements must be used in the form of calcined oxides, or with additions of partially neutralized acids. The most basic elements always react violently. In each circumstance strength is a function of reaction velocity.

In chemically setting alkali silicate bonds, the basicity of the silicate is neutralized by using acid salts of low solubility. Strongly acid salts such as calcium chloride cause very rapid setting and are useful only under certain circumstances.

Reactions After Initial Hardening

A cement must be capable of retaining its random structure during reactions which occur after the initial hardening. The primary requirements for this retention of randomness are:

- a. A gradual progress of the reaction to completion.
- b. The ability to form a new bond of network type to replace and destroyed bonds.
- c. Continued randomness of structure.

An example of what occurs when there is not a continued randomness of structure is the change from gamma to alpha alumina. This change is a slow one in nearly pure alumina, but it involves a major crystallographic rearrangement, with the alpha alumina having a highly ordered structure with essentially uniform bond strengths. The resultant mass is usually not adherent, and has little or no cementitious value.

The same is true of most hydrated salts and of the hydroxides of the larger divalent cations. These materials are not capable of replacing hydroxyl bonds with network-type bonds conforming to the requirements for random structure. Their bonds in general are of about equal strength and their dehydrations are rapid. As a result, their cementitious properties, when they occur, are destroyed by dehydration.

PHYSICAL ASPECTS OF AIR-SETTING MATERIALS

In addition to the chemistry of cements, there are other factors which must be considered in using cementitiously bonded materials. Some of these are set time, aggregate composition, surface treatment of substrate, corrosion of substrates by acids in the cement, the formation of bubbles in the cement structure, and physical properties of the formed cements.

Set Time

Reaction time has been mentioned as influencing low temperature bonding strength. It also affects the workability of the material. While a hypothetical ten-minute reaction time may be sufficient for cementation, it may not be sufficient for applying the material. This factor must be taken into account when developing a bonding material, and sufficient time must be allowed to use the material before it hardens.

Aggregate Composition

Previous mention has been made of the possible compositions of bonding materials. Since the bonded product retains in large part the properties of the aggregate, or filler, material, careful consideration must be given to the selection of these materials. The majority of munitions requirements limit the aggregate to a refractory material, which may need to be resistant to oxidizing or reducing atmospheres, depending on the application. The most popular of the filler materials are the oxides, particularly alumina, silica, and zirconia. However, silicates have also been used and the possibility exists for using nitrides and borides.

Surface Treatment

There are four theories of adherence of a ceramic to a metal which are more or less agreed upon by authorities. These may be classified generally as chemical, which has been described previously; mechanical; electrolytic, where metal oxides in the ceramic are reduced and corrode the base metal; and dendritic, where tiny dendrites of metal are formed at the interfacial zone to anchor the ceramic (Ref 7). The two latter hypotheses may be discounted as promoters of adherence in cementitious materials. While adherence of these materials is primarily due to chemical action, a small amount of adherence is due to mechanical bonding, brought about by surface treatment.

There are several methods to promote mechanical adherence. Surfaces of the substrate may be cleaned and degreased by the use of acetone or some other solvent. The surface of the substrate may be roughened, either by mechanical scrubbing or by etching with acids. Reinforcing metals in the form of screens or ribbons may be spot-welded to the substrate to provide a mechanical aid to hold the coating to the substrate.

Corrosion and Bubble Formation

One problem in using cementitious materials, especially those containing acid salts, is corrosion of the substrate and accompanying bubble formation in the coating. The bubbles are caused by gases released when the acid reduces the metal substrate. These bubbles have a deleterious effect on the physical properties of the coating, and should be prevented. For this reason, when an acid-type reaction-bonded cementitious material is developed, some neutralizer such as ammonium phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$, should be used to lessen this corrosion and bubble formation.

Properties

Physical properties of particular interest for munitions applications are adherence, hardness, and resistance to abrasion, oxidation, and moisture. It is, of course, impossible to develop all these properties to an optimum degree in one compound, but particular properties can be optimized to meet specific applications. The properties of commercially available cements will be discussed in the following section.

RESEARCH AND DEVELOPMENT OF CEMENTITIOUS MATERIALS AND COMMERCIALY AVAILABLE COMPOUNDS

Although there has been considerable research and development of ceramic cements, most of the work was directed toward developing materials for structural applications. Only recently has research been initiated to develop these compounds for use as encapsulating agents and protective coatings. Since the majority of this work was financed by private industry, much of the specific information concerning these materials remains proprietary. Thus far the military services have had limited interest in this area of material research. However the Air Force has sponsored at least two projects, described in WADC Technical Reports 55-491 and 59-102, which are entirely or in part directed toward investigation of low-temperature-bonding protective coatings and adhesives. The acid phosphates and silicate bonding materials with alumina and zirconia fillers have received the most attention.

Commercial Cements

Astroceram

A ceramic cement trade named "Astroceram" has been developed which is based on Group IV B metal oxides with a silicate bonding medium (Ref 8). Although much of the information is proprietary, the bonding medium is believed to be a reaction silicate. Astroceram is available in two types, which have melting temperatures of 4402° F and 4285° F respectively. They have a coefficient of thermal expansion of 4.11×10^{-6} in./in./° F, shrinkage of 1-4%, and density of about 175 lbs./ft³.

The more refractory Astroceram cement (m. p. 4402° F) must be heated to 1100° F to attain proper bonding, and the other cement must be heated to 2200° F. Although these formation temperatures are higher than normally expected for cementitious materials, the firing cycle is lower than a normal firing cycle for bonding these aggregates by sintering.

In the cement with the lower curing temperature, water of solution is removed at between 200° F and 250° F; then sintering at 1100° F removes bound water and induces "eutectic" bonding. Liquid phases, occurring through eutectic formation, result in densification and bonding of the body.

Bond formation occurs in the cement with the higher curing temperature similarly, but the bound water is removed at higher temperatures. In removing water at these higher temperatures, the solute present undergoes a polymerization to a number of poly-acids. Firing the material to 2200° F stabilizes the structure by eutectic bonding or by the formation of solid solutions between the polymeric acid derivatives and unreacted oxides and silicates.

This material has been successfully used as a coating and as an encapsulating agent in munitions commodities. Its main disadvantage is that it must be heated to relatively high temperatures to produce bonding.

Saureisen Cements

A series of cements (Ref 9) ranging from refractory to acid resistant to electrical-insulative are made by the Saureisen Cements Company. The aggregates include oxides, especially silica and alumina, kyanate, and silicates. Information about these cements is also proprietary, but bonding is believed to be due to alkali silicate reaction.

As would be expected with their varied specific applications, these compounds vary widely in such properties as hardness, adherence, abrasion resistance, and thermal shock resistance. Several tests were used to determine which of the compositions would be suited for coating and encapsulation applications; a number of the cements exhibited promising results. One in particular, No. 31, was used very successfully to coat traps in igniter tubes, shaped charge cones, and propellant holder rods, and to encapsulate, or "pot," thermal batteries.

These materials are true air-setting and require no heat for bonding. Set time can be varied by changing the proportions of the constituents.

Zircoa-Cast

A castable zirconium oxide (Ref 10) material which hardens by hydraulic action has been developed with the trade name of "Zircoa-Cast." It is a high-purity, stabilized zirconia refractory which has withstood short-term exposure to temperatures in excess of 5000° F, and cycling or steady-state temperatures to 4600° F.

The material shrinks less than 1% when heated to its bonding temperature of 800° F. The density of the bonded material is approximately .15 lb/cu. in. or 260 lb/cu. ft. Spall and thermal shock resistance are acceptable, but abrasion resistance and adherence to metal substrates are poor. This material is apparently intended for use in structural applications (furnaces), and has not been successfully used in coating or encapsulation applications with metals.

Phosphate-Bonded Foamed Alumina

A lightweight phosphate bonded alumina material (Ref 11) was formed by means of an acid reaction with aluminum powder in the presence of a foam stabilizer.

It was known that phosphoric acid and alumina would form a cementitious bond. It therefore seemed reasonable that a foamed material could be made by adding extremely fine aluminum powder from which hydrogen bubbles would nucleate by reaction with the acid. Wheat gluten, flour, starch, gelatin, and a commercial foam stabilizer were investigated for stabilizing the mixture and preventing collapse of the bubble structure. Ordinary cornstarch proved to be the most satisfactory.

When properly dried and cured, the material had a shrinkage of less than 1%, a density of 0.043 lb/in.³ (118 lb/ft³), thermal conductivity of 6.6 Btu in/hr ft²° F, and a modulus of rupture of 700 psi. This material can be used to a maximum temperature of 3100° F.

This foamed material could possibly be utilized as a structural material for high temperatures or as a lightweight, high temperature encapsulating agent.

A zirconia body of the same type could be formed which should permit operation at temperatures above 4000° F. This material could be used as a back up for high performance rocket parts or as a very high temperature encapsulation compound.

Air Force Research Programs

Development of Thermal Insulating Coatings

This program, as described in Wright Air Development Center TR 59-102 (Ref 12), was directed toward developing a coating that would successfully withstand temperatures of 3500° F, while providing thermal insulation and oxidation resistance for the supporting structure of a vehicle.

The first two years of this project produced several possibly satisfactory coatings, the foremost of which was phosphoric-acid-bonded alumina. In an attempt to lessen phosphoric acid attack on the steel substrate, five inhibitors were tested, methyl butynol, methylpentynol, Alkaphos E, diacetone alcohol, and ferric phosphate. Results indicated that diacetone alcohol was the most effective inhibitor; however, all of the inhibitors except ferric phosphate, had detrimental effects on the properties of the coating.

In an effort to improve adherence of the coating to the metal, a better reinforcement system was developed. This reinforcement consisted of thin, narrow, corrugated strips of metals which were spot welded to the substrate metal. Experimentation showed that steel strips 0.012 inch thick by 0.125 inch wide provided an excellent reinforcing system.

One series of compositions was formulated to evaluate the use of ceramic fibers incorporated into the ceramic coating. In coatings utilizing a sodium silicate bond, the glassy-type binder reacted with the fibers at elevated temperatures and adversely affected the coatings. The fibers were also detrimental to the phosphate-bonded coatings.

A series of coatings were made using a hydraulic setting cement having a lime-to-alumina ratio of $\text{Ca}0.2.5 \text{ Al}_2\text{O}_3$. These coatings had acceptable thermal shock resistance, but were not as hard or as strong as the phosphate-bonded coatings.

The most recent work on this project, as described in a paper by Sklarew (Ref 13), of the Marquardt Corporation, may be summarized as follows. Silicates, oxychlorides, aluminates, proprietary aluminum phosphate, silica sol, zirconia sol, borosilicates, borophosphates, phosphoric acid, and sulfuric acid were further examined as bonding media in combination with refractory metal oxides.

The usefulness of acids containing fluorine as bonding agents was also explored. These materials have the following advantages: The acid concentration for a comparable bond strength may be reduced, compositions are more refractory, setting time can be better controlled through the use of ammonium buffer salts, and heating schedules are reduced.

The experiments conducted indicated that some, and possibly all, of the monobasic, dibasic, and tribasic fluorine-containing acids may be used to bond a large excess (over stoichiometric proportion) of refractory ceramic oxides selected from the transition elements. Groups II, III, and IV, and the rare earth elements of the lanthanum and actinium series.

The two most promising coatings developed for meeting the contract requirements were:

1. Ther Marq* P-150

| <u>Composition</u> | <u>Parts by Weight</u> |
|---|------------------------|
| Al ₂ O ₃ - T61 Alcoa - 48 mesh | 50 |
| Al ₂ O ₃ - T61 Alcoa -325 mesh | 25 |
| Al ₂ O ₃ - T61 Alcoa -600 mesh | 20 |
| Red Label Clay (Ferro) | 03 |
| Mg ₂ Si ₃ O ₈ . 5H ₂ O (Mallinckrodt) | 02 |
| H ₃ PO ₄ (conc.) (Baker) | 11 |
| H ₂ O | 07 |

* Trade Name

2. Ther Marq 2 PF-100

| <u>Composition</u> | <u>Parts by Weight</u> |
|---|------------------------|
| ZrO ₂ (Norton H) -30 mesh | 40 |
| ZrO ₂ (Norton D) -325 mesh | 30 |
| NH ₄ H ₂ PO ₄ (Mallinckrodt) | 01 |
| H ₂ PO ₃ F (anhydrous) (Ozark-Mahoning) | 05 |
| H ₂ O | 02 |

This work is described in more complete detail in Wright Air Development Center Technical Report 59-102 (Ref 12).

High Temperature Structural Adhesives

This work was done on A. F. Contract No. AF 33(616)-5468 (Ref 14) to develop high temperature ceramic structural adhesives. Included in this program were the development and evaluation of an air-setting structural adhesive.

Initial work, which consisted of an investigation of a resorcinol-formaldehyde adhesive with Portland Cement, was completely unsuccessful. An exothermic reaction occurred between the materials when they were mixed, and rapid setting took place.

Some commercial adhesive compounds and sodium silicate and aluminum phosphate bonding agents with Ottawa flint, clay, alumina, zircon and carbonyl iron filler were also tested. All these materials had the serious limitations of low strength and/or low moisture resistance. However, some of the compositions, particularly the aluminum phosphate-clay-zircon, showed promise. The addition of an organic sealant such as tetraphenyltin seemed to improve moisture resistance, but more development was needed to optimize this product.

Later investigations were conducted using aluminum phosphate formulated by reacting hydrated alumina and phosphoric acid in place. Filler materials were silicon powder, carbonyl iron, copper powder, kaolin, and sodium silicate. Chromic anhydride was used in some of these adhesives as an inhibitor to prevent excessive acid attack on the substrate. Curing was at 600° F and 800° F.

Moderate strengths were achieved with the phosphoric acid-hydrated alumina composition, but bubbles in the structure limited its strength. Chromic anhydride effectively inhibited the action of the phosphoric acid, but reduced adhesion between the metal and ceramic. Substituting calcined alumina for hydrated alumina, the anhydrous phosphoric acid for phosphoric acid increased the strength.

Further tests were made using phosphate-bonded and sodium-silicate-bonded compositions. These materials were cured to somewhat higher temperatures, 1100° F to 1450° F.

The best air-setting adhesives, containing about 30 weight percent iron oxide (Fe_3O_4), were capable of developing shear strengths of about 1300 and 1100 psi at room temperature and 800° F, respectively. When such adhesives were heat treated at 1000° F to react the water present in the iron oxide, shear values dropped by about 40%. Such heat-treated adhesives, however, exhibited only a very slight further loss of strength after a 3 1/2-hour boiling water test. The same adhesives, when only air set and not heat treated, completely dissolved during the boiling water test. Results of this project indicated that shear values in excess of 800 psi at room temperature and 1600 psi at 800° F may be expected from cementitious type adhesives.

CONCLUSION

A great deal is known about the theory of cementitious bonding. Most of this knowledge has been gained through empirical research, the majority of it dealing with cementitious bonding for structural materials.

Some commercial air-setting materials have been developed for other than structural use. Cementitious ceramic materials of this type have considerable potential for applications in the munition field. These materials are well suited for encapsulation and coating applications and, to a lesser degree, for use as high temperature adhesives.

The acid phosphates and sodium silicate bonded cements appear to be the most promising. Although these materials are presently capable of meeting many of the requirements for coatings, encapsulation materials, and adhesives, further research is necessary to develop new and better ceramic cements. Adherence, thermal shock resistance, and moisture resistance must be improved, and the basic knowledge of non-hydraulic cementitious reactions must be increased if these materials are to meet munitions requirements in the future.

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