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High-Temperature Ceramic Adhesives

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Introduction

The use of organic structural adhesives for the bonding of metal structures in the aero-space industry has found increasing acceptance. Epstein[1] has listed the reasons for using adhesive bonding over the other forms of metal joining.

A barrier to the use of organic adhesives has been the temperatures imposed on structures by re-enetry and high speed flight. At temperatures in excess of 450°F., the organic adhesives break down and lose their ability to withstand long time loading.

In an effort to utilize the advantages of adhesive-bonded structures, and yet overcome the temperature limitations of the organic adhesives, research turned to the field of ceramics.

The refractory character of ceramic products is well known. This heat-resistance ability has been utilized in high-temperature ceramic coatings to protect metals from oxidation and other forms of corrosion. The ceramic coatings and their lower temperature forms—porcelain enamels—can be described as glass or oxide-base materials possessing excellent adherence and permanency of finish.

Because of the excellent adherence and high temperature resistance of porcelain enamels and ceramic coatings, these materials have been investigated for use as adhesives.

Since July 1954, when the University of Illinois Department of Ceramic Engineering began the first research on ceramic adhesives, work has been continuous in this field.

In addition to Air Force sponsorship[2-4] through their Aeronautical Systems Division, the Bureau of Naval Weapons[5] and private industry have also been investigating ceramic adhesives.

This paper will describe the preparation, application, and properties of ceramic adhesives.

Discussion

The major emphasis on the research effort in ceramic adhesives has been directed toward the development of glassy-type materials.

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Frit

The basic constituent of any glassy-type ceramic adhesive is frit. Frit is a material which has been prepared by rapidly quenching molten glass by either pouring it into water or allowing it to flow between revolving, closely spaced, water-cooled steel rolls. The quenching or fritting process produces small angular pieces of glass for the water-quenching method and small sheets of glass referred to as "flake frit" for the roll-quenching method.

To prepare frit, raw batch materials composed of oxides, nitrates, carbonates, and fluorides are mixed. Two illustrations of raw batch formulations are shown in Table I together with their equivalent oxide compositions. These particular frits (UI 117 and UI 1067) were developed by the University of Illinois. Examination of the oxide composition shows that silica is the major component and acts as the primary glass former. The alkaline and alkaline earth oxides are added as fluxes. The other materials are added or glass modifiers and auxiliary glass formers.

The thermal expansion of the metal during the bonding process and also while it is in service is a very critical point in the formulation of the frit. To maintain adherence the thermal expansion of the adhesive must closely match that of the metal.

The raw batch is charged into a heated fire clay crucible and placed in a gas-fired pot smelter at 2300°F. Figure 1 shows a representative crucible and pot smelter.

At 2300°F., the raw batch decomposes and melts to form a glass. After stirring to insure homogeneity and allowing enough time for bubbles to leave and all material to melt, the glass is fritted as already described.

Milling and Mill Additions

To put the frit in a suitable condition to be applied to metal, it must be ground and mixed with other materials in a porcelain ball mill. Figure 2 illustrates a typical ball mill and the grinding medium which consists of cylinders of sintered

TABLE I
Preparation of Frit

	UI 117	UI 1067
A. Raw Batch Formulation, Parts by Weight		
Quartz	—	24.8
Sodium nitrate	4.2	9.0
Potash feldspar	34.8	—
Borax	9.2	—
Sodium carbonate	16.5	—
Barium carbonate	0.7	—
Zinc oxide	9.2	—
Calcium carbonate	8.0	—
Sodium silico fluoride	4.2	—
Barium metaphosphate	6.9	—
Vanadium oxide (88%)	2.5	—
Aluminum oxide	3.8	—
Boric acid	—	66.2
Total	100.0	100.0
B. Equivalent Oxide Composition, Parts by Weight		
SiO_2	27.2	38.0
Na_2O	17.3	5.0
B_2O_3	4.0	57.0
Al_2O_3	13.0	—
K_2O	5.1	—
BaO	6.0	—
CaO	5.4	—
ZnO	11.0	—
Na_2SiF_6	5.0	—
P_2O_5	4.0	—
V_2O_5	3.0	—
Total	100.0	100.0

TABLE II
Ceramic Adhesive Mill Additions, Parts by Weight

	A	*B*	*C*	*D*	*E*
UI 117	100	—	—	—	—
UI 1067	—	100	100	100	—
ACA 100	—	—	—	—	100
Colloidal silica	2	2	2	—	—
Ammonium molybdate	—	—	0.8	—	—
Carbonyl iron powder	—	—	—	10	—
Silicon powder	—	—	—	10	—
18–8 stainless steel powder	—	—	—	—	20
Water	50	50	66	100	200

aluminum oxide. Porcelain balls can also be used for the grinding medium.

Collectively, the materials which are charged into a ball mill are called the mill addition. Several typical mill additions are shown in Table II. In the mill additions, the colloidal silica substitutes for the clay found in porcelain enamels and ceramic coatings by serving as a suspending agent. The ammonium molybdate shown in mill addition *C* also serves as a suspending agent.

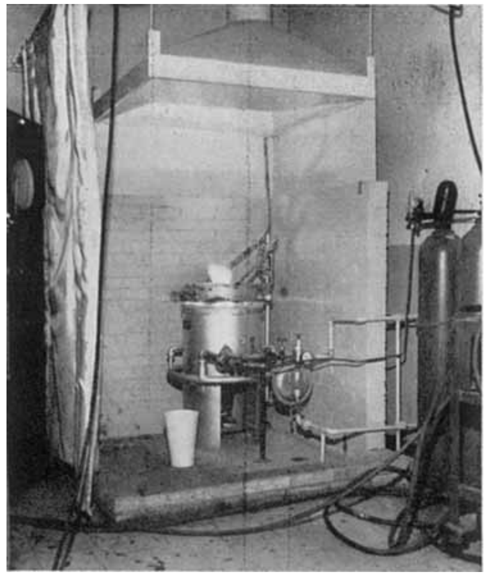

Fig. 1. Pot smelter and crucible.

Carbonyl iron, silicon, and stainless steel powders listed in mill additions *D* and *E* are added to increase ductility and strength of the joint. Common to all mill additions is the use of water as the suspending medium.

After grinding the mill addition to a point where there is only a trace of material retained on a 200 mesh screen, the mill addition leaves the ball mill as a suspension with the consistency of heavy cream. In this form, the water suspension is referred to as a "slip."

Items which must be controlled in the milling process are the fineness of grind of the frit and the specific gravity and set of the slip. Set is a characteristic of ceramic slips which controls the amount of adhesive which will be retained on an object with the specific gravity remaining constant. Set

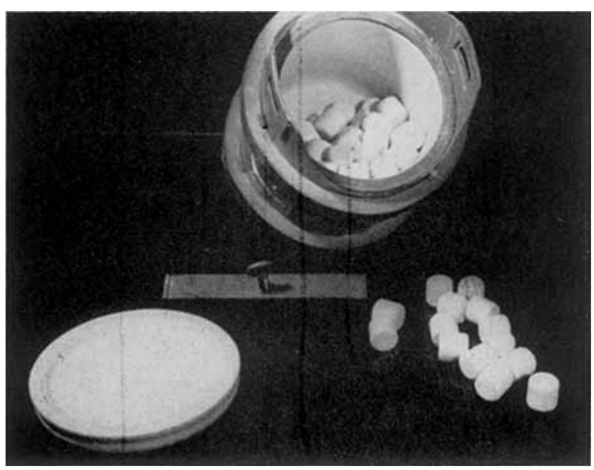

Fig. 2. Ball mill.

can be increased or decreased by the addition of electrolytes such as sodium nitrite and tetrasodium pyrophosphate. The fineness of grind is a measurement of the frit particle size. The frit particle size will affect the fusing of the glass when it is fired; the set of the slip, and the solubility of the frit. Too fine a grind, while facilitating the fusing of the frit, will raise the set to an objectionable level and may cause the frit to be excessively soluble. As a result of these considerations, a compromise must be drawn.

After the slip has been brought to a workable point, it is applied to the metal to be bonded.

Metals That Are Bonded

In general, the metals to be bonded are ones whose maximum service temperatures are in excess of those for which organic adhesives are suitable. Because of this, attention was first given to the semiaustenitic precipitation hardening steels of which 17-7PH and PH 15-7 Mo are representative. While research effort is still being done on these steels, the use temperature is rising and alloys being bonded now include the nickel-base alloys, Inconel X and René 41; cobalt-base alloys such as Haynes alloy 25, and the refractory metals. The adjustment of the ceramic adhesive for the alloy being bonded will be discussed in the section on the firing of the adhesive.

Metal Cleaning Methods

In common with all coating and organic adhesive procedures, the metals to be bonded must be cleaned. To accomplish this cleaning, the following methods can be used.

1. Sand or shot blasting. The cleaning ability of this method is well known and the surface roughening caused by the sand or shot improves the adherence of the adhesive on the metal. However, the distortion caused by high velocity particles striking honeycomb or skin would rule this method out except for relatively thick sections of metal.

2. Vapor degreasing followed by an alkaline cleaner. At Boeing-Wichita, this combination has proved satisfactory for laboratory specimens.

3. Acid etching. A $HF\text{-}HNO_3$ acid etch has also been used.

Application Methods

Spraying, dipping, and brushing are used to apply the ceramic adhesive. As noted before, the set and specific gravity can be adjusted to help control the amount of adhesive that is applied. The application weight is controlled so as to give the thinnest application consistent with adequate coverage.

Drying and Firing

Before firing, the adhesive must be dried. This drying can be done at room temperature but it is preferably done at 250°F.

After drying, the articles making up the joint are mated and pressure applied. Pressures in the range of 25–50 psi are used. Figure 3 shows the two halves of a typical lap shear joint with the dried adhesive applied. The piece of metal foil between the two halves is brazing alloy. This combination of ceramic adhesives and brazing alloys will be discussed later.

Figure 4 shows two lap shear specimens placed in a firing jig which is designed to maintain joint positioning during the firing process.

The firing jig, with specimens in place and a pressure plate in position over the lap areas, is placed in a furnace. Figure 5 shows the fixture in a furnace.

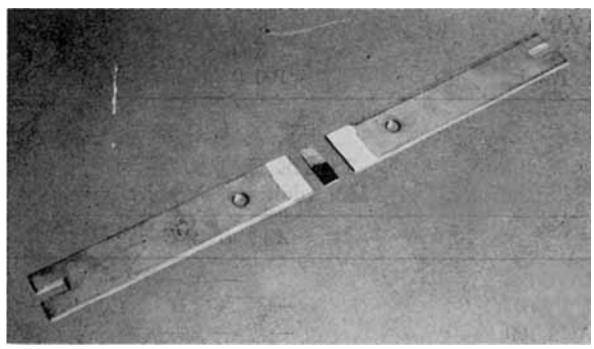

Fig. 3. Lap shear specimen with ceramic adhesive applied.

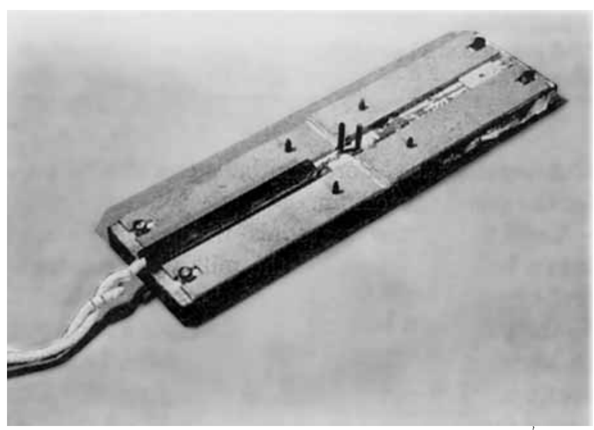

Fig. 4. Lap shear specimens in jig ready for firing.

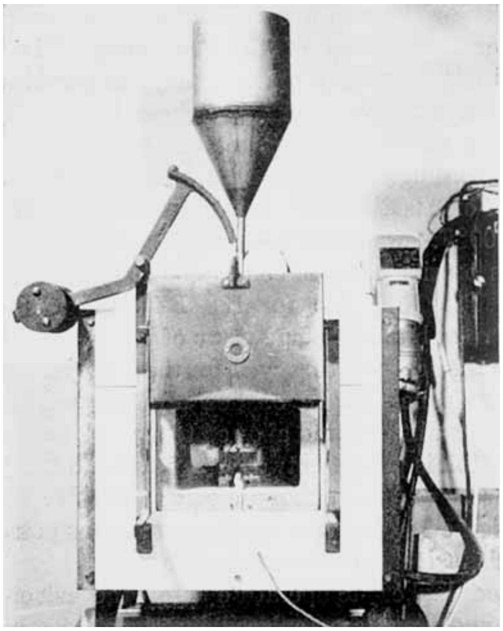

Fig. 5. Firing fixture in furnace.

Pressure is applied to the joint by a stainless steel rod protruding through the top of the furnace. The amount of pressure can be changed by varying the amount of lead shot placed in the container located on top of the rod. The joint is then fired at a temperature and time necessary to cause the adhesive to fuse.

On cooling, the adhesive solidifies and causes the joint to be bonded. The firing temperature is determined by the frit composition. Ideally, this firing temperature is adjusted to coincide with the heat treating cycle for the metal being bonded. As an example, the adhesives for 17–7PH and PH 15–7 Mo steels are formulated to fire at 1750°F. This temperature is used in the austenite conditioning step for the RH 950 heat-treat cycle for these steels.

A rule of thumb used in ceramic coatings and one which is usable for ceramic adhesives is that the firing temperature of the adhesive must be 200–300°F. higher than the maximum use temperature of the metal being bonded. At temperatures from 200–300°F. below the firing temperature of the adhesive, the glass softens and cannot support load. An examination of the use temperatures for refractory metals shows that the glasses used for bonding these metals must fire in the 2500–2800°F. range. Accordingly, highly refractory glasses must be used for these metals. The normal silica-base glasses used for other metals are not suitable and alumina- and tantalum-base glasses are being investigated.

Properties of Ceramic Adhesives

The glassy type of ceramic adhesive and those partially modified by the addition of metallic powders possess the following characteristics.

1. Brittleness. The brittleness of glassy-type coatings is well known. However, this property does not become a limiting factor as evidenced by the widespread use of porcelain enamels and ceramic coatings. The brittleness can be reduced by maintaining as thin a coating as possible and also by design of the part. As the part is subjected to elevated service temperatures, this brittleness is reduced due to the softening of the glass. This softening makes the joint more pliable.

2. Increase in strength as service temperature is increased. The ceramic adhesives increase in strength as the service temperature is increased. This is illustrated by Figure 6. The strength of a typical organic adhesive is also shown for comparative purposes. It can be seen that this strength increases up to maximum from which point the strength drops off rapidly. This is due to the glass

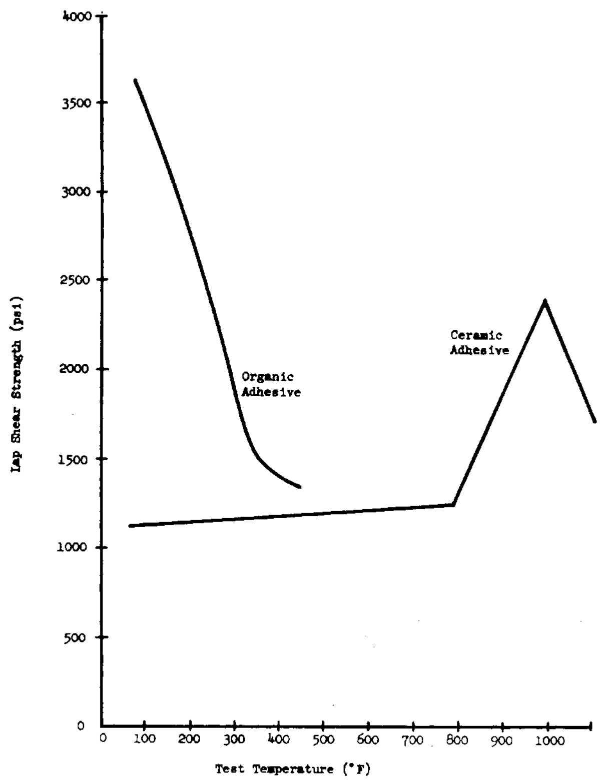

Fig. 6. Elevated temperature lap shear strength for representative organic and ceramic adhesives.

softening to a point where it cannot support the load. This maximum use temperature, if not the same as the maximum use temperature of the metal being bonded, can be adjusted by formulating the frit to mature at a higher temperature. This adjustment of formulation is limited, however, by the heat-treating temperature range of the metal.

Ceramic Adhesive-Brazing Alloy Combinations

As noted previously, ceramic adhesives are brittle. In addition, the lap shear strengths are not as high as those found with brazing alloys. In the temperature range where brazing alloys are suitable, the present state of the art for ceramic adhesives does not make these materials competitive with brazing.

The brazing alloys, while possessing ductility and higher strengths than the ceramic adhesives, have the big disadvantage of requiring protective atmospheres and/or vacuum in order to produce the bond.

The Wichita Branch of The Boeing Company has developed a process which utilizes a combination of ceramic adhesives and brazing alloy to bond superalloys. A patent application has been made covering this development.

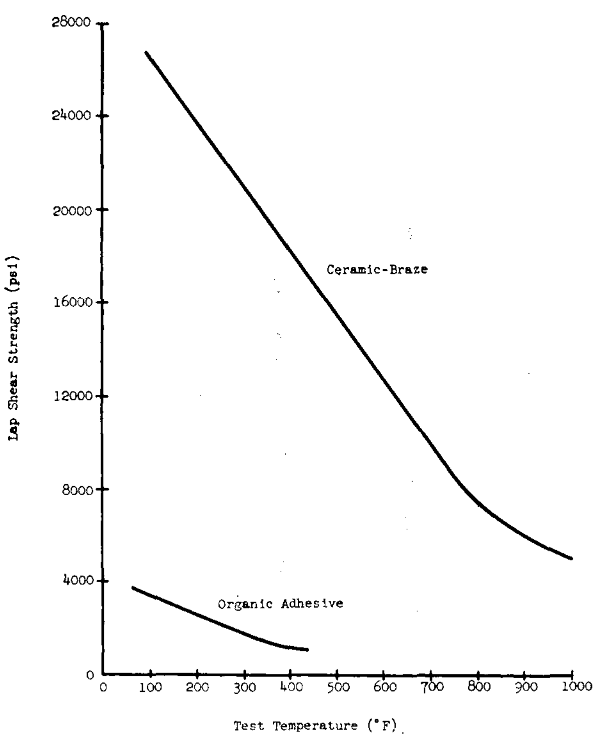

Fig. 7. Elevated temperature strengths of representative organic adhesive and ceramic-braze adhesives.

Two systems are currently being investigated under sponsorship of the Air Force. The first uses the silver-base brazing alloys in combination with a ceramic adhesive. These brazing alloys have a maximum use temperature of 800°F.

Accordingly, a silver-base brazing alloy in the form of 0.002 in. foil—maximum use temperature of 800°F.—was selected for the preliminary work. This brazing alloy is being used to braze 17–7PH and PH 15–7 Mo for the B-70 program. Its optimum brazing temperature of 1750°F. coincides with the heat-treating cycle for these alloys.

The panels to be bonded are sprayed with a ceramic adhesive and allowed to dry. The brazing alloy foil is placed between the joint and the joint is then fired in air under pressure at 1750°F.

Figure 7 shows the lap shear strengths possessed by this system at various temperatures.

For higher temperature use, the silver-base brazing alloys are replaced by nickel-base alloys. These alloys have a maximum service temperature of 1500°F. and are commonly furnished in the form of powders. The brazing alloys powders are mixed with the ceramic adhesive slip in the ratio of 80 parts of brazing alloy to 20 parts of ceramic adhesive (dry weight) and the resulting slurry brushed on vapor-degreased metal panels. The joints are fired at 2000°F. to produce the bond.

Advantages of this combination of ceramic adhesives and brazing alloys over conventional brazing methods are:

1. No need for protective atmospheres and/or vacuum to produce the bond.

2. Cleaning and handling methods are simplified. It has been found that no increase in strength is brought about by the use of all alkaline cleaners and acid etches when compared to vapor degreasing alone. The handling with gloves of cleaned metal surfaces is not required.

3. Machining tolerances for honeycomb core of 0.005 in. can be used compared to the 0.003 with conventional brazing. The cost savings resulting from this relaxation of tolerances amounts to approximately $20.00 a square foot.

4. Tooling costs are lower.

5. The use of perforated and nonperforated core is possible without changing the process. The use of perforated core is preferred in conventional brazing in order to allow the inert gases to flow to all parts of the structure. In areas of honeycomb used for fuel storage, perforated core cannot be used because of the possibility of fuel leakage through a hole in the skin.

Other Types of Ceramics Adhesives

In addition to the glassy-type ceramic adhesives, other types are being investigated.

1. Air setting adhesives. Refractory materials which were primarily designed for use as refractory cements are being used. They include aluminum phosphate, sodium silicate, and spark plug cement.

2. Devitrified ceramic adhesives. These adhesives utilize a devitrified glass to produce the high temperature strength. By partially changing the structure of the bond from a glass to a crystalline materials, the softening effects of the glass are lessened and higher temperature strengths are possible.

3. Exothermic ceramic-metal adhesives. A development by Narmco Industries[6] uses an exothermic reaction to produce a metal bond. The glass phase is squeezed out of the joint.

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Synopsis

This paper describes the preparation, application, maturing, and fired properties of ceramic adhesives. The great majority of ceramic adhesives are based on a glass-type bond similar to that found in porcelain enamels and ceramic coatings. Using a frit as the basic constituent, the adhesives are applied to clean metal surfaces and fired to produce the bond. The adhesives resulting from this process retain a useful strength at temperatures of 1000°F. or higher. A process for combining ceramic adhesives and brazing alloys is also described. This combination has produced joints superior in strength to straight ceramic adhesives and comparable in strength to standard brazed specimens.

Résumé

On discute dans cette publication les préparation, application, mise en forme et propriétés à la cuisson des adhésifs céramiques. La grande majorité des adhésifs céramiques sont basés sur des liens de types vitreux semblables à ceux trouvés en émaux de porcelaine et en recouvrement de céramique. En employant une fritte comme constituant de base, on applique les adhésifs sur les surfaces de métal propres et on porte à la cuisson pour produire le lien. Les adhésifs résultant de ce procédé conservent une force utile à des températures de 1000° F. et des températures plus élevées. On décrit aussi un procédé de combinaison des adhésifs céramiques et des alliages (soudés). Cette combinaison a produit des joints supérieurs en force aux adhésifs céramiques habituels et comparables en force aux spécimens classiques soudés.

Zusammenfassung

In der vorliegenden Mitteilung werden Darstellung, Anwendung, Reifung und Eigenschaften im gebrannten Zustand von keramischen Klebstoffen beschrieben. Der überwiegende Teil der keramischen Klebstoffe beruht auf einer glasartigen Bindung, wie sie etwa in Porzellanemail und keramischen Überzügen vorliegt. Mit einer Fritte als Grundbaustein werden die Klebstoffe auf reinen Metalloberflächen zur Anwendung gebracht und zur Herstellung der Bindung gebrannt. Die nach diesem Verfahren erzeugten Verklebungen behalten bei Temperaturen von 1000°F. oder höher eine brauchbare Festigkeit. Weiters wird ein Verfahren zur Kombination keramischer Klebstoffe und Hartlotlegierungen beschrieben. Diese Kombination liefert Verbindungen, deren Festigkeit den einfachen keramischen Klebstoffen überlegen und den hartgelöteten Standardproben vergleichbar ist.

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